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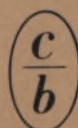
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LITHOLOGY AND MINERAL RESOURCES

A translation of *Litologiya i Poleznye Iskopaemye*

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Publication therefore did not occur prior to this date, but must be assumed
to have taken place reasonably soon thereafter.*

In the article, the author presents an overview of the large amount of material available on the structure of the island-arc systems on the periphery of modern oceans. The fundamental elements of these systems, their development, and the character of the sedimentary and volcanogenic-sedimentary deposits formed within them are discussed. It is suggested that such an overview will facilitate the discovery of paleoanalogs preserved in fragmentary fashion within the folded belts of the continents.

Rock associations similar to those occurring in modern island-arc systems associated with active continental margins exist in the folded belts of the continents. Such associations have a cardinal significance for establishing the character of geosynclinal basins in general, since they are definite structural reference points. A comparison of the island-arc complexes of geosynclines and modern, active continental margins is gradually being carried out, but the project is of a fairly general character and fundamental attention has been given to the petrochemistry of vulcanites rather than to sedimentary infilling. It is known that modern island-arc systems have a complex structure and a definite tendency in their development; moreover, there is a certain range of variation among them (there are different types of arcs). The above mentioned facts demand a more detailed comparative-lithological analysis. For this purpose, it is first necessary to consolidate the data of modern island-arc systems and their sediments. Information concerning the dimensions of the systems and their elements, which would be impractical for a study of folded regions due to the peculiarities in their tectonic structure, take on important significance.

An overview of appropriate material from the literature is provided in this article. It is hoped that the article will aid in interpreting the island-arc complexes of the past, their structure, disposition, and structurofacies conditions of formation.

We will confine our attention to problems associated with sedimentation. We will not concern ourselves with dynamic models of the creation and evolution of island arcs. Many reports are concerned with these models, and, although alternate approaches are given in them, the pivotal point is almost always an acknowledgement of subduction [8, 13].

The principal elements of island-arc systems are: deep-water trenches, the rises or island arcs (s. lato), and the back-arc basins (tylovye kotlovini)* or marginal seas. Rises includes volcanic ridges (island arcs s. str.) and arc-trench transitions. Not all marginal seas belong to island-arc systems [20], but it has been rightly emphasized [20] that the majority of them are spatially close to and genetically associated with the latter, and that the two should be considered together. Active interarc basins, which could be equally categorized with island-arc rises and marginal seas, illustrate this point well.

Trenches, as a rule, are situated on the outer, oceanic side of a rise, but, in rare, special cases, they are located on back side of a rise (New Hebrides, Solomon Islands).

Several classification schemes of island arcs have been proposed. Different investigators have approached this problem in different ways. If classifications based upon the theoretical assumptions of authors are excluded, the chief criteria upon which the classification of island arcs are based become the basement's character, age, and position within the con-

*In English-language publications, "kotlovina" is rendered by the term "basin," but this does not correspond to the accepted meaning of the latter ("bassein") in the Russian language. Back-arc basin refers to a basin rather than marginal sea, and the latter may consist of several back-arc basins ("basseinov").

continent-ocean system. These criteria correlate in the majority of cases. V. E. Khain [14] classified arcs into young intraoceanic arcs (for example, Mariana, Melanesia), usually expressed by a small number of small, broken-up islands, and mature arcs representing fragments of complex folded structures which have experienced several cycles of geosynclinal evolution (Kamchatka, Kapan). These later arcs are isolated from the continent by comparatively large-scale marginal seas. Investigators of the Pacific margin of Asia have suggested classifications which are similar in essence [6, 11, 23]. K. F. Sergeev [11] distinguished between near-continental and intraoceanic arcs; a pseudooceanic type including the Melanesian arc, characterized by trenches not only in the front but also in the back area of the system, was also identified. Other geologists have given most of their attention to the nature of the basement when attempting classifications. In some arcs, the basement is sialic; in others, it is mafic. A granitogneissic layer is present in the first case, but is absent in the second. Arcs have also been noted with a heterogeneous basement (the Aleutian). "Sialic" arcs "coincide" with near-continental and mature types, while "mafic" arcs coincide with intraoceanic and young types.

Let us turn our attention to the relationship between volcanic arcs and marginal seas [9]. Active basins (with clearly expressed spreading) are associated with young arcs (Mariana, Bonin, New Hebrides, Tonga-Kermadec); while inactive basins are associated with more mature arcs located nearer to a continent.

Differences exist in the overall structure of island-arc systems. Along the northern and central areas of the eastern border of Asia, they have an "orderly character" and the mainlands are festooned with them. Large marginal seas are associated with the island arcs. In the seas of Southeast Asia, they form a small complex mosaical system together with island arcs and microcontinents. The width of the system (from the Yap Trench to the Philippine Trench) is more than 3000 km.

Trenches

The depths of the trenches vary from 4.5 to 11 km, widths are 100 ± 50 m, and lengths are from 500 to 2000 km [13, 21]. The inner (near-island) slopes are steep ($3-6^\circ$ above, $15-28^\circ$ below) and complicated by wave terraces with widths from 18 to 75 km and lengths of up to 130 km. The outer (near-ocean) slopes of the trenches are gentle ($1-2^\circ$), with large-scale faults forming a system of small horsts and grabens. The bottoms of the trenches (0.5-20 km) are flat. The thickness of the sedimentary cover varies within the trenches: in individual cases, the trenches are "semidesolate" (thicknesses < 100 m); other trenches are filled with sediments 2-3 km deep.

The sedimentary infillings of the trenches have been penetrated by a small number of boreholes, but one can piece together a conception of these sediments from dredging and seismic-profile data.

The trenches of the Pacific rim have been the most studied. Their total length is almost 30,000 km, and more than half of the sediments belong to the categories of "desolate" and "semidesolate" ("starved"). The thicknesses of the sediments here range from insignificant to 400 m. They lie toward the western margin of the ocean and are separated from the continent by frontal (located at the trench-arc transition) and back-arc basins, which are traps of sedimentary material. The remaining trenches, the eastern near continental trenches, have, with several exceptions,* thick (1-2.5 km) sedimentary infillings.

The sediments in the western trenches are primarily pelagic and hemipelagic. Usually, they are greenish diatomaceous-clayey muds, sometimes with admixtures and intercalations of ash. In several intervals, predominately in the Miocene, their quantities increase (tuffites). The quantity of terrigenous fragmental material is somewhat less; such material is usually silt. Sandy material and packets of turbidites (the Japan Trench, Hole 440) appear only locally in the upper portion of the section. In general, they are uncharacteristic of the western trenches.

In the eastern trenches, from the Chilean Trench to the central sector of the Aleutian Trench, the section has a two-member structure.

*An exception is, for example, the sector of the Peruvian-Chilean trench situated near the Atakama desert; the sedimentary infilling of the trench here is < 50 m.

The lower stratum was formed by relatively fine sediments, often hemipelagic or pelagic (clayey and diatomaceous muds), but, in several cases, packets of silty clays appear with intercalations of graded silts which are considered distal-turbidite formations. The thickness of the stratum is usually appreciable (200-400 m), but the thickness reaches 1.3 km where silty packets are present. The age of the portion of the section under consideration includes the Middle-Late Cenozoic and, sometimes, the Early Cenozoic.

The upper stratum is distinguished by a coarser composition. Its structure and thickness can vary even within a single trench, but the overall character of the stratum is constant everywhere. The primary background of the sections consists of irregularly stratified terrigenous deposits: clays with intercalations of silts and fine-intermediate grained sandstones, more rarely, coarse-grained sandstones. Individual intervals are more clayey, and the silts within them constitute only 5-10% of the total. The silts form 0.5- to 2-cm layers. Other intervals are more saturated with silts and sandstones. These rocks constitute up to 60% of the section and have thicknesses of 5-40 cm [29]. Organogenic detritus carried in from the shelf and the slope and also shells of foraminifera and coccoliths (including some reworked from older strata) are present within them. The preservation of the carbonate material, despite the depth below the carbonate-compensation level, can be explained by the rapid sedimentation. Ashlayers and intercalations enriched with diatoms are sporadically present.

This stratum is generally identified as a "turbidite wedge" [29, 34]. The comparatively finely fragmental material, despite the depth below carbonate-compensation, can be explained by the placement of the boreholes of the section within major distributory channels. Thus, in the axial portion of the eastern sector of the Aleutian trench, seismic researchers have discovered a fairly wide and gently sloping channel located 500 m from Hole 180 and dissected by 470 m of distal turbidites.

The thickness of the turbidite wedge is appreciable (0.5-1.5 km), especially if one keeps in mind that the wedge was formed within a comparatively short stretch of time (the Quaternary).

In places, individual sectors of the trenches are completely or almost completely filled with sediments. The major portion of these sediments can be classified as turbidites. Sometimes, they spill out onto the abyssal basin of the ocean to a distance of more than 100 km. This is the case, for example, with the southern portion of the Chilean Trench and the northern Central-American Trench located in the region of the Astoria submarine cone [34].

Seismic profiling established that the turbidite deposits lie horizontally or on a gentle slope, but that the lower (hemipelagic deposits) are tilted toward the side of the continent.

The Ellin Trench (the Eastern Mediterranean Sea) is substantially different with respect to dimensions and depth (4650 m). Holes drilled in the trench cut through 480 m of Quaternary sediments. The lower portion of the section was formed primarily by nannofossiliferous marls (grey and olive-grey with iron sulfides). Thin clayey and silty intercalations are present in the marls. The upper portion of the section is a rhythmic interstratification of sands, silts, and marls. The sands are polymictic, with reworked shells of benthic foraminifers. The stratigraphic and textural features indicate deposition of the material by along-trench turbidite flows and bottom currents. Two horizons with reworked sapropelic material were noted [32].

In general, two groups of deposits are characteristic of the trenches. The first include pelagic and hemipelagic sediments with compositions determined to a significant degree by the location of the trench in one or another climatic zone, distance from the distributive province, and depth. The second group are represented by terrigenous fragmental complexes (turbidite-contourite). In the majority of cases, the latter tend to occur toward the tops of the sections. Many sediments are enriched with ash to various degrees.

In some trenches where there are no thick turbidite deposits, chaotic, deformed accumulations have been discovered by seismic profiling at the foot of the inner slope. These accumulations are considered by some to be a product of a caving-in of the trench wall and are considered by others to be a result of a "scraping" of the sediments and rocks of the oceanic platform during subduction. There is very little actual data on the compositions of these accumulations. They are usually supercompacted, fissured, deformed trench sediments (stations 181, 298 of the Deep-Sea Drilling Project), sometimes with lumps of carbonate rock (site 127, Deep-Sea Drilling Project).

Arc-Trench Transitions

The zone between the front of a volcanic arc (s. str.) and the break in the slope of the trench has been named the arc-trench transition. Its width is approximately 175 ± 75 km (up to 450 km in individual cases) but can be small (50-70 km). Thus, it is commensurate with the width of a trench and volcanic ridge. The break in the slope of the trench is frequently marked by a rise of the acoustical basement formed by the deformed layers. The rise can be expressed as an insular ridge (at Sumatra) or as a submarine elevation (a depth of 2.5-3.5 km), but sometimes it is weakly manifest in the relief because of burial under sediments. In the rear portion of the transition, the frontal basin (or a chain of pans and troughs) forms terraces when filled with sediments.

The arc-trench transition has a sedimentary mantle of complex structure. This has been established primarily by seismic profiling. Two complexes are clearly distinguishable on the profiles: an "accretionary" complex and a "frontal-basin" complex.

The first complex occurs on the outer portion of the transition and can usually be traced on the inner slope of the trench. The deposits here are deformed into folds overturned toward the side of the ocean and broken up by listric faults in the opposite direction. Thus, the entire complex is a series of plates inclined toward the arc; a pattern of increasing ages of deposits can be detected in this direction. The deformed complex can be thought of as an accretionary prism or wedge; the proposed accretion of material to the arc massif and growth of the complex on the oceanic side reflects this terminology. The deformed rocks are in contact along a sharp separation surface with undeformed oceanic rocks which are interstratified for tens of kilometers under the frontal portion of the prism (see Fig. 1). In some systems, there is no accretionary prism (the Mariana Arc) or the prism is weakly expressed. This is apparently connected with the absence of large sedimentary accumulations in the frontal portion of the arc. Large-scale accretionary prisms are also known in regions where trenches are not expressed geomorphologically (the Makran continental margin and the region of the Lesser Antilles) [18, 39].

Many models exist for the formation of accretionary prisms [1], but a discussion of these models is not in line with our task. Usually the formation of the prisms is associated with subduction and compression by rises.

The accretionary complex has been well studied with regard to structure (seismic profiling), but data on the composition of the deposits is limited. We will present two examples: Japan and the Lesser Antilles.

The pertinent deposits have been penetrated by boreholes on the inner slope of the Japan Trench (stations 434, 435, 440, and 441). The width of occurrence of these deposits is 25 km, reckoned from the axis of the trench.

The chief components of the sections are: aleuropelites and clayey diatoms with various, sometimes appreciable ash contents. Sandy turbidites occur in the upper portions of the slope. It is characteristic that the sediments of the lower and upper portions of the slope are lithified at a shallow depth and bear traces of tectonic brecciation and cleavage. A fourfold repetition of stratigraphic horizons (diatomaceous zones) was noted in one of the boreholes (site 434). Methane is present 180 m below the bottom surface. Dacitic clastics (island-arc) represented by boulders are disseminated along the entire section. Thus, the Japan accretionary prism was primarily formed from terrigenous, hemipelagic, and pyroclastic material. Judging from the seismic profiles, such deposits locally form large slide masses (site 435 is located on a slide). It has been noted that there are no accumulations in the Japan Trench which have been "planed" off the oceanic platform [33].

The second example is of an accretionary complex occurring east of the Lesser Antilles islands and called the Barbados complex. Its width has been estimated to equal from 80 km in the north to 450 km in the south, and the maximum thickness varies from 10 to > 20 km [38]. As pointed out, a deep-water trench is not expressed in this region, and the accretionary prism borders with the basin of the open ocean along the deformation front. Holes 541 and 542, located in the "distal portion" of the accretionary prism, were drilled 3 km to the west of the latter. In Hole 541 (a water-depth of 4950 m), 459 m of sediments were discovered down to the Lower Miocene. The section is represented by two tectonic units separated by a fault at a depth of 276 m. The uppermost of these includes deposits from Recent to Upper Miocene, the lower of the two includes deposits from the Middle Pliocene to the Lower Miocene. A repetition at a larger scale was discovered at several levels. Brecciation, deformation, and slickenslides are present in places.

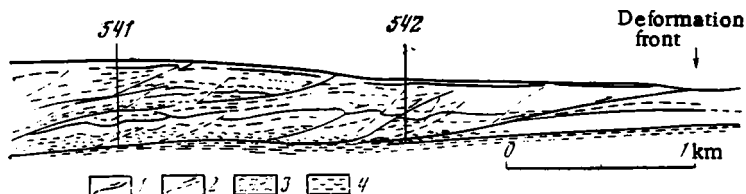


Fig. 1. Profile through holes 541, 542, and the deformed front of the Barbados Crest complex (put together from results of drilling and data from seismic profiling). 1) faults discovered by drilling; 2) proposed faults; 3) squamate structure; 4) sediments pushed under the surface of disruption (the vertical scale equals the horizontal scale).

A large portion of the section was formed in various degrees by clayey nannofossiliferous muds and, more rarely, by foraminiferous muds; a packet (30 m) of lower Middle Miocene yellowish-brown radiolarian aleuropelites occurs only in the very lowest portion of the section. Intercalations of ash (1-7 cm) occur along the entire section. The deposits were formed under calm, deep-water conditions near the lysocline, and only the early Miocene layers are below the carbonate compensation depth. The absence of terrigenous turbidites should be kept in mind [18].

The material presented is of interest first, with regard to the fact that they confirm the seismic data on the dislocated nature of deposits in the accretionary prism and second, with regard to the fact that the prism was entirely formed of pelagic and hemipelagic sediments, in contrast to the Japanese example.

Deposits of the same accretionary prism found on the island of Barbados (southwest from the region of drilling activity) are assigned to an area near the South American continent.

The section here is significantly different from that discussed above. It was formed by two strata which differ with respect to facies. The lower stratum (the Scotland suite of Paleocene-Eocene age) is represented by the terrigenous deposits of a submarine debris cone, and the upper stratum (an "oceanic series" of Eocene-Miocene age) is represented by siliceous-carbonate pelagic and hemipelagic formations. Both strata are deformed and (as in the other cases), the inner portion of the prism (the portion more distant from the ocean) is thicker and includes more ancient layers.

Clay diapirs and mud volcanics are characteristic of the prism. They are found in the ocean near the deformation front. One of the volcanoes has a height of 60 m, and a cross section of 2 km. Its crown portion is located several hundred meters from basaltic basement. The formation of the mud volcanoes is connected with the pressure of pore waters migrating along permeable horizons under the influence of the weight of the accretionary mass [38].

The second complex, the *frontal-basinal* complex differs from the preceding horizontal or gently sloping bedding of the deposits infilling both the large-scale depressions (basins) and shallow troughs. Basins with widths of up to 100 and even 200 km are known. Their depths are various (up to 4 km), but a general tendency toward shallowing is noticeable. Many depressions are filled entirely with sediments, in which case the bottom takes on a flat relief. The thickness of a complex can reach a few kilometers (1.5-6 km). On seismic profiles, these stratified strata are usually interpreted as turbidites. The complex lies either on rocks of the arc massif, on the accretionary prism, or on the area of transition between the massif and the prism.

Drilling indicates that the deposits are different in different regions. Hemipelagic and pelagic sediments predominate in individual regions, while terrigenous turbidites are of great importance in others. We will present several examples.

A stratum (256 m) of predominately nannofossil deposits which are clayey or ashy to various degrees lie on a volcanic basement in the frontal basin of the Mariana Arc (hole 458, a water depth of ~3.5 km). An admixture of biogenic silica (diatomaceous, radiolarian) occurs in some intervals, chiefly at the top of the section. Vitric and crystallovitric ash is present along the entire section, but in various quantities. This ash is present not only in the form of an admixture, but also in the form of authigenic intercalations. The ages of the deposits are from Pleistocene to early Oligocene. Several discontinuities have been found. The

presence of 1.5-cm pebbles of sedimentary and volcanic rock (Oligocene nannofossils can be found in the fragments) is associated with one of them (early Miocene).

The deposits of the frontal basins may have undergone substantial lateral alterations. The Mariana example illustrates this. Not only homogeneous nannofossiliferous marls and chalk but also thick (475 m) turbidite accumulations represented by an alternation of marls and volcanoclastic silts and sandstones constitute the principal portion of the section in Hole 459 (near the outer margin of the basin; a water depth of 4100 m) east of Hole 458. The presence of slide horizons and neptunian "minidikes" is characteristic.

The more northerly sections illustrate another characteristic of the deposits.

Thus, a siliceous-terrigenous turbidite stratum consisting of silty and ashy diatomaceous muds alternating with volcanoterrigenous sands consisting of andesitic and basaltic clastics with small admixtures of felsic clastics was discovered (hole 186, a water depth of 4.5 km) in the Aleutianian terrace (a filled frontal basin); minerals of greenstone alteration (epidote, amphibole) are present in small quantities. The distributive province was the Aleutian Crest.

In the frontal Hidaka basin located east of the Tokyo (Japan) Arch, boulder-pebble clayey conglomerates and breccias (47 m) consisting of fragments of dacite and siliceous argillites formed as a result of the scouring of lower-lying Cretaceous rocks lie on the scoured surface of the Upper Cretaceous (holes 438, 439) [37]. They are covered by a packet (105 m) of massive quartz-feldspathic sandstones and aleuropelites with abundant mollusk detritus. The age of the packets is Oligocene.* The next interval (143 m) is an alternation of black and olive-grey sands, silts and clays (a turbidite stratum) replaced upwardly by clayey deposits with intercalations of ash and limestones. The age is early-to-middle Miocene. A stratum (866 m) of dark-grey and olive clayey-diatomaceous sediments with ash intercalations and limestone concretions occurs above these feldspathic-quartzose sands and silts are present in the top portion of the section.

The section presented is evidence of rapid loading of the region and a change of conditions from subaerial to shallow-water-sea in the Oligocene, to midbathyal (depths of 500-1500 m) at the beginning of the Miocene, to deep-bathyal (2000 m) in the Pliocene. A shallowing began starting from the Pliocene. The depths are 1500-1600 m at the present time [37].

In general, the infilling of the frontal basins is formed of hemipelagic (biogenic, clayey) ash and terrigenous fragmental material. Accumulations of sapropelic matter sometimes occur here [21]. The deposits of different regions vary depending upon the bathymetry and climatic environment. The great thicknesses of the deposits, and sometimes the structure of the sections, indicate a tendency to subsidence; however, the high rate of arrival of sediments not only compensates for the rate of subsidence, but exceeds it; this results in a shallowing. The occurrence of active volcanic arcs (sources of clastics) and an outer structural rise making the frontal basin a sedimentary trap exerts a cardinal influence upon the sedimentation.

Volcanic Arcs (s. str.)

The elongated belts which constitute the archipelagos of active and extinct island and submarine volcanos are volcanic arcs in the strict sense of the word. Sometimes they form twins (the Kurile ridges) or bifurcate (the Lesser Antilles Archipelago). In such cases, the volcanism of the outer ridges was more ancient than that of the inner ridges.[†] The volcanic archipelagos were sometimes entirely created by magmatic processes and include not only volcanic formations but also co-genetic plutons and sometimes volcanoes situated on large island massifs consisting of complexly deformed ancient geosynclinal strata (Japan). The term *arc massifs* was introduced for them [23]. Volcanic arcs are sometimes classified as *arc orogens*, as opposed to *collision orogens* [22].

*There is evidence that the sandstones were brought not from the volcanic arc but from the ancient Oyashio rise situated to the east. The remains of this rise are located under the upper portion of the inner trench slope at the present time [37].

[†]The outer ridge in the Lesser Antilles arc was active in the Eocene-early Miocene, but the inner ridge has been active from the later Miocene to the present day.

Besides active arcs with active volcanoes, more ancient volcanic submarine ridges where eruptive activity has recently ceased exist in some systems. They are usually interpreted as portions of former frontal arcs separated from the active arc as a result of interarc spreading during the evolution of the system as a whole. These arcs are classified as relict arcs. They usually are situated within marginal seas and form submarine ridges.

The ejected rocks of the arc have received a great deal of attention. Geochemical indices of island-arc magmatic series have been established; in the majority of cases, this allowed the discovery of the rocks in the ancient fold belts. The rocks are generally differentiated complexes. Many petrologists distinguish three series among them; island-arc tholeiitic, calc-alkaline, and alkalic [31]. The first includes basalts, andesites (islandites), and a number of dacites. The SiO_2 content is from 48 to 63% in the majority of cases. The second series is characterized by andesites and dacites with small quantities of rhyolites; the SiO_2 content is 52-70%. The third series has a lesser significance and is represented by both a sodium group and a potassium, shoshonite group. Tholeiite is absent in some systems, and there is reason to believe that this holds true for ensialic island-arcs [17]. A transverse petrological asymmetry (an increase in the potassium content with increasing distance from the trench) is noticeable for both the effusive and intrusive phases of the magmatism. This may be useful for palinspastic reconstructions in folded regions.

The volcanoes of island-arcs have large coefficients of explosiveness and have supplied large quantities of volcanoclastics to zones of sedimentation. These zones constitute substantial portions of volcanic edifices and includes many diverse genetic types of deposits, both terrestrial and marine. They have received serious attention from lithologists and a thorough overview by L. N. Botvinkin [2].

The histories of the volcanic arcs are determined by alternations of constructive and destructive phases. The first phases were accompanied by an activation of magmatism and growth of the volcanic edifice; the next phases were accompanied by denudations of the latter and, sometimes, by subsidence.

The Aleutian Crest, including the island, is a good example in this regard [35, 36]. The constructive phase (pre-Oligocene) was associated with an accumulation of lavas ranging from basaltic to rhyolitic. Tholeiitic and calc-alkaline varieties can be distinguished. Sediments are few. The stratum includes granodiorites and small bodies of gabbro. The rocks have undergone thermal metamorphism. The volcanic growth of the crest decreased or ended during the Paleogene-early Miocene times and a destructive phase lasting 10-13 million years began. Sub-aerial denudation of the islands, abrasion of the apical platforms of the crest and canyon "plowing" of the slopes of the crest were associated with this phase. An overall subsidence of the crest was also a feature of this phase. The crest became differentiated during this time; graben-like depressions infilled with thick (up to 1 km) sediments appeared. Initially, these were, at least in part, subareal formations; then marine formations - volcanomictic and pelagic (diatomaceous) - were included. A new constructive phase began 5-6 million years ago, when "volcanic growth" came to predominate over disintegrative forces.

Erosional-abrasional processes and the abundance of easily scoured, loose tephra led to the appearance of abundant volcanoterrigenous and tephroidal materials. These were deposited both upon the near-island shelves and upon the submarine slopes of volcanic ridges in neighboring depressions. The coarser clastics and sediments contain shelly material. Deposits of gravity flows (volcanomictic turbidites and tephroturbidites) are widespread within the boundaries of the slopes.

A stratum (50 m) of Upper Pliocene penetrated by a borehole (stations 457, a water depth of 2647 m) can serve as an example of the deposits in the subsided areas of the active crest. This stratum is located on the Mariana Crest between the Pagan and Alamagan islands. The deposits are represented by coarse sandstones with intercalations of crystallovitric ash containing a carbonate admixture (foraminifera and nannofossils). The sandy fraction is formed of cinnamon-brown glass and plagioclase. Dacitic material is present. Judging from seismic profiles, such deposits belong to a fairly thick stratified layer which pinches out toward the islands.

On the West-Mariana crest (a relict arc), boreholes pass through the Upper Miocene represented by an alternation of vitric tuffs of various grain sizes, volcanomictic breccias, and conglomerates. The stratum is unevenly stratified. Individual packets are more thinly bedded (layers <10 cm); massive beds with thicknesses of 4.5 m are present in other packets. The

tuffs contain skeletal detritus of shallow-water species (corals, gastropods, large foraminifera) and also lignite fragments. Fragments consist of basalts and andesites. The sedimentation rate is very high (400 m/million years).

Foraminifer-nannofossiliferous muds of Pliocene-Quaternary age (a thickness of 36 m) occur above the fragmental stratum.

Volcanoclastic deposits are not the only deposits associated with active crests, but they are especially characteristic. Reefs and other carbonate deposits arise on the slopes and tops of submarine volcanic structure under appropriate climatic conditions. They are especially characteristic of subsided relict arcs (the Colville-Lau and Palau crests as well as others); however, they are found on the submarine portions of active arcs, having formed predominately during the periods involving a drop in volcanic activity. Limestones, for example, make up the "platform" on the slope of the outer ridge of the Tonga Crest; they extend along the crest for 400 km. They were formed at depths of approximately 300 m, but are located 4 km below sea level at present; this indicates great subsidence. Limestones lie upon ejected rocks (basalts, gabbros, and peridotites), and are interstratified with volcanoclastic sediments. The maximum carbonate accumulation decreased during the late Eocene, Miocene, and Pliocene-Pleistocene [24]. Limestones are present on the islands of Bonin, Guam, and Saipan, which are elevated areas of the frontal portions of island-arcs (Iwo-Jima and the Mariana). These shallow-water reefogenic strata with thicknesses of up to 400-500 m lie on top of volcanic rocks. Their age in the Bonin islands is Eocene and younger; their age in the southern islands is Miocene-Pleistocene [24].

Thus, an abundance of volcanic and subvolcanic rocks of specific compositions, rocks which can be interstratified and combined with volcanogenic-sedimentary (fragmental) rocks, are characteristic of volcanic arcs (s. str.). With increasing distance from the volcanic centers, terrigenous and volcanoterrigenous deposits of various grain sizes take on evermore importance. Both shallow-water, shelf accumulations with radiolarian detritus and clearly stratified turbidite strata occur along them. The latter form both on the periphery of the volcanic ridges and within their boundaries, infilling the depressions between volcanic islands.

The turbidite strata include the usual basinal sediments: hemipelagic and pelagic. Depending upon the climatic zonality, their differences are fairly clearly manifest. They are represented by diatomaceous sediments at high latitudes and by carbonates at low latitudes.

Marginal Seas

Marginal seas are fairly diverse with respect to size, morphology, history of development, and, possibly, mechanism of formation. Various models for their formation have been proposed [10]. Discussion of these models is not part of our objective. The most popular models are ones involving a spreading at the rear of the island arc [9] and a model involving preservation of the oceanic crust during the formation of the arc [3]. It is possible that both processes are involved in the histories of some seas. The marginal seas for the western Pacific Ocean are grouped into three types [16]: 1) a type involving back-arc spreading; 2) a type formed during rifting at the continental margin (South-China, Tasmania); 3) a type of unclear genesis (Sulawesi, Sulu). Since island-arc systems are being discussed in this article, our primary attention will be focused on the first type.

Marginal seas can have depths commensurate with the abyssal basins of the open ocean (5-7 km); however, they are generally less deep. In the Sea of Japan, for example, the largest depressions reach 3-3.7 km, but several do not exceed 2-2.5 km. The near-continental shelves are narrow in some cases but broad in others and may cover a major portion of the basin (Bering, Okhotsk) [7].

The marginal seas themselves are complicated by large and small internal, usually submarine rises which divide the seas into a series of bathyal and abyssal basins possessing oceanic crust. Individual rises have the shape of isometric blocks with large flanks and faulted benches (it has been suggested that many of these are broken and extended fragments of continent crust [4]); others are interstratified in the form of crests. These are subsided relict arcs; their ages show a pattern of decrease in the direction from continent to ocean. Back-arc basins are located between the crests. D. Karig [9] distinguishes between the active (interarc) and inactive basins among them. In the first type, spreading is continuing at present; spreading has ceased in the second type.

The Mariana Trough and Lau Basin are examples of active basins. They are each located between an "active" volcanic ridge (the Mariana and the Tonga, respectively) and a relict arc (the West-Mariana and Colville-Lau crests). The widths of the basins are small (100-400 km); the depths differ but are less than in the neighboring basins of the open ocean (up to 2 km or more) and less than in adjacent, inactive back-arc basins (up to 1-2 km). In the axial portions of the structures under consideration, the sections are represented by two strata: volcanic and sedimentary. The first consists of massive and pillow tholeiitic basalts with intercalations of pelagic and hemipelagic sediments (limestone muds, ashy aleuropelites, and clays). The second (the Mariana Trough, hole 454A) consists of greenish silty and ashy clayey muds with intercalations of crystallovitric ash. Several intervals are enriched with biogenic material: nannofossils and diatomaceous and radiolarian remains. The thickness of the stratum is 67 m. The age is late Pleistocene. Closer to the active volcanic ridge, the sedimentary section is represented by volcanoterrigenous deposits (gravellites and contourites) with intercalations of ash and pumice. Drift of the material takes place from the side of the active arc [19].

An unusual section passes through the inner flank of the Mariana Trough (site 453). Two strata are also found here. The lower stratum (149 m) is primarily represented by schistose and brecciated serpentinites and gabbro under which breccias occur. In the power portion of this stratum (30 m), the breccias are fragments of metamorphosed andesites and dacites; in the upper portion (85 m), there are fragments of gabbro diabases, and basalts. The material is unsorted and slightly worked. Individual fragments reach 45 cm in size. The binding mass consists of finely comminuted clastics of the same composition; there is a great deal of carbonates, chlorite, iron oxides, and clayey minerals within the binding mass; quartz, epidote, and prehnite are also present. The fragmental material belongs to rocks of the island-arc series [25]. They were metamorphosed and sometimes subjected to tectonic forces up to the point of the formation of the breccia itself. The clastics apparently entered from the slope of the West-Mariana Crest and the metamorphism preceded the formation of the trough. The breccia itself is most likely a slumped mass (olistostrome) created in the fault zone [25]. The upper sedimentary stratum (455 m) is a sandy-clayey turbidite layer. The fragmental fraction is primarily volcanitic. Toward the top, the quantity of sandy material decreases and deposits enriched in biogenic silica appear.

The deposits of the interarc basins are fairly similar to the deposits of the other depressions associated island arcs with respect to composition (an abundance of volcanomictic turbidites and hemipelagites). However, the section as a whole is distinguished by the presence of tholeiites with intercalations of pelagic sediments in the lower portion. The sedimentary infilling of the interarc basins is asymmetrical because of the great inflow of volcanoterrigenous and pyroclastic material from the active arc. Some tendency toward a sinking of the basin over time occurred, as indicated by the increasing role of fine muds. Probably, this is due to the widening of the structure which resulted from the spreading.

The majority of basins of marginal seas of the western periphery of the Pacific Ocean are classified as "inactive," many of these were created as a result of back-arc spreading, however, their traces are far from always preserved. The spreading origin can be inferred indirectly in such cases according to the similarity of the structure of the basin with the structures of undoubted spreading events.

One of the best examples of an inactive "spreading structure" is the Parece-Vela basin (the Philippine Sea). It is bounded by submarine crests: the West-Mariana to the east and the Kyushu-Palau to the west (relict arcs). In the central portion of the basin, the remains of an axial rift active in Middle-Tertiary times [4, 28] are interstratified parallel to the crest. The depth of the major portion of the basin is approximately 5 km, but the depth is more than 6 km in the rift troughs. The basement of the basin is represented by fresh and altered tholeiitic basalts. A peculiarity of the basin is its isolation from the inflow of terrigenous fragmental material from the continent. The deposits of the western and eastern portions of the basin have characteristic differences.

A small (111 m) sedimentary stratum (Upper Oligocene-Pleistocene) occurs in the west (Hole 449) above pillow basalts. Yellowish-brown nannomuds are present at its base (~14 m). Higher in the section, the stratum is represented by eupelagic brown clays in which intervals enriched with radiolarians and nannofossils forming authigenic intercalations are present.

In the eastern portion of the basin (Hole 450), the sedimentary stratum is thick (330 m) and consists of two units. The lower (Middle Miocene, a thickness of 250 m) was formed by a

monotone stratum of predominately fine vitric, often argillized tuffs with sparse intercalations of coarser tuffs (sandy and large grain sizes). Diverse sedimentary textures are present: slanted and horizontal layering, signs of intrusion, and a gradational distribution of material. A small admixture of biogenic carbonate (coccoliths) is common. The rate of sedimentation was 50 m/million years. The upper unit (Middle Miocene, a thickness of 83 m) is represented by brown clays (ashy to various degrees) and intercalations of ash in the lower half of the section. The rate of sedimentation was slightly higher than 2 m/million years [28]. The volcanic material constituting the major part of the section arrived from the Mariana arc; the thickness of the clastic stratum increases in the direction of this arc. The relict, subsided arcs were not such important "suppliers" of sedimentary material, however, slides are associated with them in places.

In contrast to the Mariana interarc trough, eupelagic rather than hemipelagic sediments predominate in the Parece-Vela basin. This was a result of the large opening and the large amplitude of subsidence associated with the "old" structure. Moreover, the overall features associated with the formation of sedimentary cover are abundantly and visibly expressed in its asymmetrical structure. Thick volcanomictic shelves developed in the frontal portions of the basins in both cases. Such a pattern was first discovered by D. Karig [9] and is probably useful for investigations in ancient folded regions.

In seas cut off from the continental inflow of material, fragmental sedimentation is almost entirely due to drift from volcanic ridges. The thicknesses of the tuffo-volcanoterrigenous associations near such ridges can reach several kilometers, but the thickness of the stratum at the bottom of the depression (a stratum in which hemipelagic and pelagic sediments already have taken on substantial importance) decreases (a few hundreds of meters or less). In narrow interarc troughs, the shelves of volcanoterrigenous deposits can reach the spreading zone and lie directly upon basalts. Such deposits are often superseded by pelagic (or hemipelagic) muds common for the given sea.

In seas located directly alongside a continent or other large areas of land (Japan), sedimentation is complicated by an abundant inflow of terrigenous material. Thus, in the South China Sea, where the large rivers of Asia empty, the accumulation of terrigenous material is so intensive that it leads to progradation of the continental slope [26]. In the Sea of Japan, not only is the continent a supplier of clastics, but the Japanese islands as well. The terrigenous material arrives from the shelves through canyons and valleys to the feet of the slopes, thus forming fan systems. Stratified sandy-silty-ashy strata with thicknesses of several hundreds of meters are formed here [15].

Thus, the following groups of a facies complexes can be distinguished in the sedimentary mantle of marginal (back-arc) seas: 1) fragmental volcanomictic turbidite (an interlayering of tuffs, volcanic sands, silts, and pelites (clays and ash) deposits. The formation of this complex occurred on the periphery of volcanic island rises, including the slopes, feet, and sometimes, the adjacent portion of the basin; 2) fragmental polymictic deposits of the same type, but associated with a continent (or large islands rises); 3) silty-clayey deposits, with the participation of one or another quantity of biogenic material (it covers the foot areas of the basin and is closely associated with the previously mentioned complex). This complex can be classified with hemipelagic and distal-turbidite deposits; 4) essentially siliceous (radiolarian, diatomaceous) deposits which are pelagic and hemipelagic sediments (clayey-siliceous); 5) essentially calcareous, pelagic deposits; 6) "red" clays formed at deeper water levels.

Pyroclastics are present in almost all of the complexes, sometimes in very minor amounts, but several intervals of the section are enriched with them. Ash (glass, crystalloclastics) are present in the "red" deep-water clays of young active back-arc basins (Mariana, Lau) in various, sometimes significant, quantities. This distinguishes them from the abyssal clays of the open ocean and the older back-arc basins of the marginal seas [26]. These "early clays" can be picked out by rate of accumulation (30-50 m/million years), since the usual rate of sedimentation of red clays is 2-3 m/million years.

The following volumetric relationships involving various types of deposits [27] were calculated for the back-arc basins of the western Pacific Ocean: slides (debris flows), 1.2%; turbidite foehn systems, 25.7%; hemipelagic and distal-turbidite clays, 21.8%; pelagic clays, 4.2%; biogenic siliceous-pelagites, 4.3%; biogenic pelagic carbonates, 23.8%; reworked carbonates, 9.5%; pyroclastics, 3.5%.

As is well known, many marginal seas are complicated by internal rises varying in form, size, and origin. Their peaks are usually located at depths below 1 km, often at approximately 2-2.5 km, but individual eminences reach 600 m [12]. Several of the rises are devoid of unconsolidated cover. Accumulations of coarse material consisting of fragments of local basement rocks are present. However, where the sedimentary mantle is significant and penetrated by boreholes, it is represented by pelagic and hemipelagic sediments muds entirely or to a significant degree.

Small en bloc crests (Daito, Gogia, and others) and plateaus (Amali, Benham, and others) are known to exist in the western portion of the Philippine Sea [4].

Thus, hole 445 penetrated deposits up to the Middle Eocene (~900 m) in a small depression (depth of water 3400 m) on the Daito Crest (depth of water 2000 m). Two strata were distinguished.

The lower stratum (242 m) was a sandy-conglomeratic stratum beneath coarser material. Consistently increasing amounts of silts, clays, and nannofossil limestones appear upward in the stratum. The conglomerates are unsorted, angular, and poorly rounded. Pebbles of altered greenstone rock (alkalic basalts, andesites, and gabbro), sometimes constituting 90% of the coarse fraction, predominate. Pebbles of chalky reefogenic limestones are present. The sandy material is formed of clastics of the same type. However, there are many minerals here (plagioclase, pyroxenes, olivines); chrome spinel and minerals of greenstone alteration can be pointed out. Diverse organogenic detritus and large benthic foraminifera are locally abundant. The conglomerates are coarser in the lower part of the section (fragments of up to 15 cm). Their beds are thick (up to 5 m), and they show a chaotic distribution of sand and pebbles. A slide origin is attributed to them. The dimensions of the pebbles (up to 1.5 cm) and the thicknesses of the layers decrease upwards. A gradational structure is evident. The sandy-silty packets separating the layers have textures characteristic of turbidites.

The upper stratum (650 m) is carbonate in nature, consisting primarily of nannofossil muds and chalk with intercalations enriched with foraminifera, clayey material, and ashy material. Bioturbation is widely occurring, but the textures characteristic of turbidites are preserved in places. The occurrence of such intervals is connected with increases in the rate of sedimentation and the processes associated with reworking of the material. It is calculated that approximately 60% of the latter are reworked.

Hole 292 on the Benham plateau passes through a sedimentary stratum (367 m) from the Eocene to the Quaternary represented by chalk with small quantities of silica and nannofossil muds. The sedimentary section on the Kyushu-Palau crest (Site 296) is also represented by a thick (453 m) stratum of nannomuds and chalk.

The presence of carbonate sections is generally characteristic of the rises. This is due to the location of the bottom above the CCD. Clayey-diatomaceous muds with intercalations of ash occur on the rises (Yamato, Bauers) to the north.

* * *

It is evident from the material presented above that the sedimentary mantle of the island-arc systems is formed by characteristic, interrelated complexes of deposits (associations). The materials composing the associations are polygenic, therefore, the associations are identified by the predominant component. The following associations are the most widely occurring.

1. A terrigenous fragmental (turbidite) association consisting of an alternation of sands, silts, and clayey muds. Gravel-pebble intercalations are possible in the proximal portions. The fragmental material is polymictic, including a "sialic" component and sometimes an "island-arc" component. Clastics are associated with a continental source or large areas of island land. Turbidity flows and bottom currents, creating submarine-fan systems (foehns), have great importance in the formation of the deposits. The associations are primarily characteristic of marginal seas (the continent foot and the adjoining basin) but are present in trenches near the continent. The thickness of the association varies with a range of 250 to 900 m. The rate of sedimentation indicated is approximately 100 m/million years. However, the thickness can reach several kilometers (judging from seismic profiling data) where the deposits belong to the proximal portion of the cone.

2. A volcanomictic (turbidite) association formed by an alternation of volcanoterrigenous and terrigenous sands, silts, gravels, ash, and clays. Carbonate and siliceous mater-

ials may be present in subordinate quantities. The association makes up the submarine shelves near the island volcanoes which are the sources of clastics (explosions, scouring of structures). Gravitational processes (turbidity s. lato) and bottom currents are of great importance in the transport and deposition of fragmental material. The rates of sedimentation are high (350 m/million years and more). Thicknesses sometimes reach 2-3 km. The associations are characteristic of interarc and back-arc basins, frontal depressions, and some trenches. The deposits are the chief component of many accretionary prisms.

3. The hemipelagic associations include several interrelated varieties differing in the makeup of components included. One of these varieties is almost completely terrigenous: silty-clayey, partially containing material from distal turbidites. Fine-grained sands are present in such associations. Other associations contain, in addition, ash and biogenic material. They may be present in great quantities, both by forming of admixtures to terrigenous sediments and by forming authigenic units in the associations; ashy-clayey associations and also strata of more complex compositions, respectively, can be distinguished. The thicknesses of such associations vary over a wide range: from several tens of meters to 900 meters and, in special cases, more. The rate of sedimentation is comparatively low (10-100 m/million years); however, the rate can increase, for example, during an abundance of ash. The composition of the biogenic sediments are determined by climatic zonality and bathymetry in the final analysis. Siliceous muds are associated with global bands of silica accumulation; carbonate muds are associated with the tropical zone and areas with bottoms above the CCD.

Hemipelagic associations are present in the depressions of all the elements in the island-arc systems: in trenches, and in frontal and back-arc basins, including precontinental depressions. They enter into the compositions of accretionary prisms and, in rare instances, occur on rises (the Yamato crest).

4. The pelagic carbonate association is represented by foraminiferous-nannofossiliferous muds (or chalk) with subordinate quantities of clayey material (marls and intercalations of clay) and sometimes ash. Siliceous intercalations and concretions (siliceous-carbonate intervals) are present in places, radiolarians and sponge spicules can be identified within them. The thickness of the carbonate association varies from a few meters to 400 m, and the rate of sedimentation varies from 10 (rarely less) to 100 m/million years. The association is usually present in marginal seas cut off from the major inflow of terrigenous material. It coincides with relatively shallow (4.7 km and less) basins and rises separating them, including the subsided portions of volcanic ridges.

5. Pelagic "red clays" occupy a very modest position with respect to volume in island-arc systems, but their formation encompasses significantly long time intervals in certain zones. The conditions of formation of this characteristic type of oceanic sediment has been well investigated [5], as has been their composition. Eupelagic and miopelagic clays (transitional to hemipelagic) can be distinguished among them. Moreover, "early" and "late" clays can be differentiated by studying the composition and structural position of the clays in a system of island arcs [26]. Early clays are enriched in ash; there is a relatively high content of montmorillonite within them, and sometimes biogenic components. Their rates of sedimentation are somewhat higher (30-50 m/million years) than those of abyssal clays. They form during the early stages in the development of interarc basins. The "late" clays are similar to abyssal clays and are present in well developed (wide) back-arc basins.

Polymictic sandy-conglomeratic and brecciated accumulations of significant (250-450 m) thickness are also found in island-arc systems. They have a small distribution in comparison to other deposits and occur in marginal seas on the rises (the Daito crest, an elevation in the New Hebrides trough) or near rises (the Parece-Vela basin near the Kushyu-Palau crest). Coarsely fragmental deposits usually coincide with the basement of the sedimentary mantle.

In the tropical zone, reefogenic structures and shelly-detrital limestones are locally associated with rises (tomentose fragments of volcanic arcs, etc.). Slide and turbidite carbonate accumulations coincide with slope facies (according to the calculations of Klein and Lee [27], they constitute 9.5% of the sedimentary mantle of the back-arc basins of the Pacific island arcs).

Besides the sedimentary and volcanic-sedimentary associations enumerated, volcanic and sedimentary-volcanic complexes are present in island-arc systems. These include, firstly, an effusive tuffaceous complex (including a subvolcanic body and packets of volcanomictic deposits) belonging to volcanic ridges, and secondly, basalts, frequently of the pillow variety, apparently marking spreading centers (or oceanic crust "entrapped" during the formation of the arc).

The material presented on the composition and structure of the principal rock associations of modern island-arc systems and their displacement within the various structural-morphological zones of these systems can apparently be of aid in establishing paleoanalogs which which have been fragmentarily preserved in the folded belts of the continents. A number of difficulties arise in this connection; they are associated with the fact that similar and near-by associations present seem to have disappeared and are present in different zones. Finding the ages for the associations can probably be an "aid" here. In developing island-arc systems, one must expect a "younging" of the association from the inner to the outer portions of the system.

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A new estimate is obtained of the quantity of solid materials entering the ocean from river runoff. The distribution is cited of runoff of suspended and traction loads over continents and oceans. Average long term data on solid runoff for 436 rivers are utilized for the calculation, and this method is applied to local extrapolation.

An accurate estimate of solid and dissolved materials entering the ocean from dry land has great value for correct understanding of the processes of terrigenous sediment formation in seas and oceans. Terrigenous sedimentary material enters sedimentary basins from river and glacial runoff, as a result of shore erosion, and by eolian transport. In agreement with existing data, solid river runoff exceeds all remaining sources of detrital material by more than 5 times, and exerts a determining effect on sediment formation in seas and peripheral portions of the ocean, that is, in regions of avalanche sedimentation [4, 5].

Inconsistent estimates of the quantity of sedimentary material entering the ocean from land annually have been obtained since 1950. These vary from 12.69 to $51.10 \cdot 10^9$ tons. A critical review of these estimates is conducted in [4]. One of the recent estimates of solid river runoff presently assumed in the theory of global oceanic sedimentogenesis is $18.53 \cdot 10^9$ tons/yr, calculated by A. P. Lisitsyn [4]. This estimate, well as estimates by other investigators, was obtained in the following manner. The solid runoff of suspended loads from the major rivers of the drainage area (the reliable determinations of river stations) was totaled for each ocean, from which the average modulus of suspended sediment was determined (the ratio of the total solid runoff to the total area of the considered river basins) for the drainage areas included in observations. Extrapolation of this modulus over every oceanic drainage area yielded the quantity of total solid runoff into the ocean. In the estimate thus obtained ($18.53 \cdot 10^9$ tons/yr), data from 40 river basins were utilized (61% of the overall drainage area) for the Atlantic and Arctic oceans, 9 river basins (42%) for the Pacific Ocean, and 8 river basins (39%) for the Indian Ocean. Due to the low frequency of reliable determinations, the runoff of traction loads was completely neglected.

Thus, the applied method has two evident inadequacies: 1) the neglect of traction load runoff; and 2) the extrapolation of the average modulus of solid runoff of the studied territories over the entire oceanic drainage area. It is known that oceanic drainage areas are the largest geomorphological subdivision on a planetary scale; they are extremely nonhomogeneous in their landscape-climatic conditions, geologic-geomorphologic structure, and the degree of Quaternary alteration of natural landscapes. Therefore the tolerated (so called global) extrapolation may lead to significant error in the estimate of overall solid runoff, particularly into those oceans whose drainage areas are insufficiently characterized by reliable data of hydrologic stations, while these are unevenly distributed over the drainage area. Nonetheless, the calculated estimate of solid river runoff included practically all available reliable determinations of river stations, and the method of its acquisition entirely satisfied the existing level of knowledge on erosion and runoff of loads on the Earth.

Much new data on the erosion and runoff of loads has appeared in recent years. A. P. Dedkov and V. I. Mozzherin [3] conducted a thorough review. This article is based on observations of the runoff of suspended loads at 3763 points. An estimate of erosion on the plains and in the mountain regions of the Earth was given, the dependences of erosional intensity are derived based on the climate and landscape, the sizes of the drainage area and relief, the geologic structure (rock composition), and man's agricultural activity. A map of the runoff of suspended loads on the Earth was composed, and the erosional structure of the river

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TABLE 1. Solid River Runoff into the Global Ocean from the Territory of Europe

Basin (ocean)	Sector	Drainage area, 10^6 km ²	Suspended loads, 10^9 tons/yr	Traction loads, 10^9 tons/yr	Av. modulus of suspended load runoff, 10^9 tons/km ² /yr	Ratio of traction loads to suspended loads	Total solid runoff, 10^9 tons/yr
Arctic	Nonrunoff region (Arctic islands)	0,131	0	0	0	—	0
	From the Severnaya Dvina river basin to the Urals	0,652	0,011	0,0007	16,9	0,06	0,0117
	Western basin of the Severnaya river	0,748	0,002	0,0001	2,7	0,05	0,0021
	Total	1,531	0,013	0,0008	8,5	0,06	0,0138
Atlantic	From the Kuban river basin to Varna	2,048	0,004	0,015	45,9	0,16	0,109
	From Varna to the Po river	0,328	0,122	0,027	372,0	0,22	0,149
	From the Po river basin to the Pyrenees Peninsula	0,325	0,242	0,053	744,6	0,22	0,295
	Pyrenees Peninsula	0,585	0,468	0,103	800,0	0,22	0,571
	From the Pyrenees Peninsula Baltic sea basin	0,855	0,013	0,002	15,2	0,15	0,015
	The Baltic sea basin	2,060	0,007	0,0004	3,4	0,06	0,0074
	Mediterranean islands	0,066	0,020	0,005	303,0	0,22	0,025
	Great Britain and Ireland	0,314	0,007	0,0004	22,3	0,06	0,0074
	Remaining islands	0,188	0,0006	0,00004	3,2	0,06	0,00064
	Total	6,769	0,974	0,205	143,9	0,21	1,179
	Global	8,3	0,987	0,2058	118,9	0,21	1,193

TABLE 2. Solid River Runoff into the Global Ocean from the Territory of Asia

Basin (ocean)	Sector	Drainage area 10 ⁶ km ²	Suspended loads, 10 ⁹ tons/yr	Traction loads, 10 ⁹ tons/yr	Av. modulus of suspended load runoff, 10 ⁹ tons/km ² yr	Ratio of traction loads to suspended loads	Total solid runoff, 10 ⁹ tons/yr
Arctic	Nonrunoff regions (Arctic islands)	0,129	0	0	0	—	0
	From the Urals to the Yana river basin	9,943	0,067	0,004	6,7	0,06	0,071
	Yana river basin river and eastwards	1,600	0,040	0,009	25,0	0,22	0,049
	Total	11,672	0,107	0,013	9,2	0,12	0,120
Atlantic Pacific	Asia Minor, Caucasus, and islands	0,627	0,231	0,051	368,4	0,22	0,282
	From Chukotka to the Huang He river basin	4,240	0,062	0,010	14,6	0,16	0,072
	From the Huang He river basin to the Indochina Peninsula	3,239	2,966	0,475	915,7	0,16	3,441
	Indochina Peninsula	2,091	0,594	0,131	284,1	0,22	0,725
	Sakhalin	0,076	0,009	0,001	118,4	0,16	0,010
	Japan islands	0,370	0,070	0,015	189,2	0,22	0,085
	Islands of the Malay archipelago	1,889	0,536	0,118	283,7	0,22	0,654
	Total	11,905	4,237	0,750	355,9	0,18	4,987
Indian	Basins of the Ganges and Brahmaputra rivers	1,640	2,240	0,493	1366,7	0,22	2,733
	Southern Asia	3,430	1,803	0,288	525,7	0,16	2,091
	Southwest Asia	1,710	0,060	0,010	35,1	0,16	0,070
	Sri Lanka	0,066	0,012	0,003	181,8	0,22	0,015
	Islands of the Malay archipelago	0,150	0,079	0,017	526,7	0,22	0,096
	Total	6,996	4,194	0,811	599,5	0,19	5,005
Global		31,200	8,769	1,625	281,1	0,19	10,394

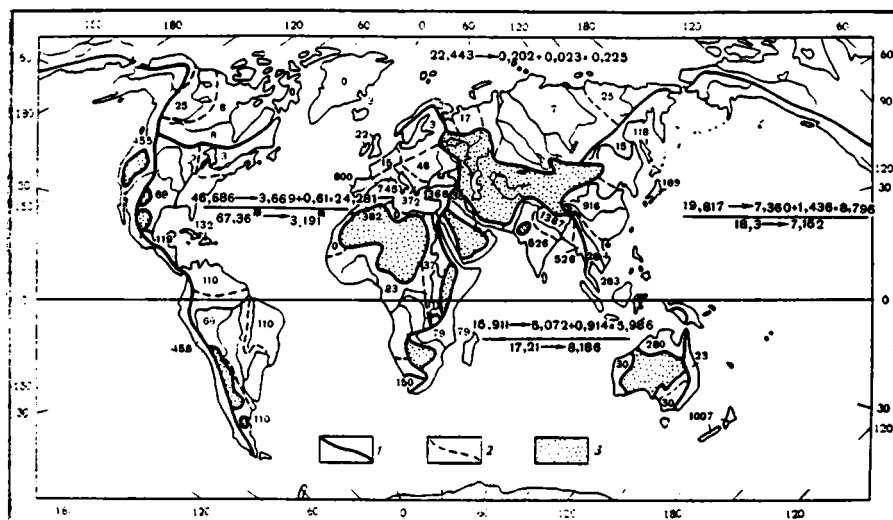


Fig. 1. Solid river runoff into the Global Ocean: 1) boundaries of oceanic drainage areas and regions of internal runoff; 2) boundaries of sectors in which solid runoff calculation was conducted; 3) regions of internal runoff (the numbers refer to the sectors: the average modulus of suspended load runoff, calculated at determined hydrological stations). The numbers within the limits of oceanic water area are the drainage basin areas and the calculated values of solid river runoff in the following sequence: in the numerator is the area of the drainage basin (without Antarctica), $10^6 \text{ km}^2 \rightarrow$ suspended load runoff (10^9 tons/yr) + runoff drawn from bow (10^9 tons/yr) = solid river runoff (10^9 tons/yr); in the denominator, for comparison, from A. P. Lisitsyn's data [4], is the area of the drainage area, (without Antarctica) in millions of $\text{km}^2 \rightarrow$ suspended load runoff (10^9 tons/yr). Asterisks denote the total value for Atlantic and Arctic oceans.

TABLE 3. Solid River Runoff into the Global Ocean from the Territory of Africa

Basin	Sector	Drainage area, 10^6 km^2	Suspended loads, 10^9 tons/yr	Traction loads, 10^9 tons/yr	Av. modulus of suspended load runoff, $10^3 \text{ tons/km}^2 \text{ yr}$	Ratio of traction loads to suspended loads	Total solid runoff, 10^9 tons/yr
Atlantic	Nonrunoff regions	0,990	0	0	0	—	0
	Nile basin	2,870	0,106	0,006	36,9	0,06	0,112
	Atlas	0,540	0,206	0,045	381,5	0,22	0,251
	Equatorial Africa	9,510	0,219	0,035	23,0	0,16	0,254
	Southern Africa	1,020	0,153	0,024	150,0	0,16	0,177
	Total	14,930	0,685	0,111	45,9	0,16	0,796
Indian	Continent	5,020	0,395	0,063	78,7	0,16	0,458
	Madagascar and other islands	0,590	0,046	0,007	78,0	0,16	0,054
	Total	5,610	0,441	0,071	78,6	0,16	0,512
Global		20,540	1,126	0,182	54,8	0,16	1,308

basin, the relationship of traction and suspended loads, and their granulometric composition were thoroughly analyzed. In particular, it was established that even in the limits of a single landscape-climatic and orographic zone, the runoff of suspended loads may vary significantly in dependence on the composition of the rock in the drainage area and the degree of its Quaternary alteration. Simultaneously, the boundaries and areas of the oceans and drainage basins were redefined [6]. All this makes possible a more accurate estimate of the quantity of runoff entering the ocean, not only of suspended river loads, but also of the traction river loads. This is the first to obtain an estimate of the overall solid river runoff.

TABLE 4. Solid River Runoff into the Global Ocean from the Territory of North America

Basin	Sector	Drainage area, 10 ⁶ km ²	Suspended loads, 10 ⁹ tons/yr	Traction loads, 10 ⁹ tons/yr	Av. modulus of suspended loads runoff, 10 ³ tons/km ² yr	Ratio of traction loads to suspended loads	Total solid runoff, 10 ⁹ tons/yr
Arctic	Nonrunoff regions (Arctic islands)	2,740	0	0	0	—	0
	MacKenzie river basin	1,770	0,044	0,007	24,9	0,16	0,051
	Remaining territory	4,730	0,037	0,002	7,8	0,06	0,040
	Total	9,240	0,082	0,009	8,9	0,11	0,091
Atlantic	Nonrunoff regions (Arctic islands)	0,879	0	0	0	—	0
	From the Labrador Peninsula to the Hudson river basin	1,800	0,006	0,0003	3,3	0,06	0,0063
	From the Hudson river basin to the San Juan river	5,530	0,382	0,023	69,1	0,06	0,405
	Central America	0,630	0,075	0,012	119,0	0,16	0,087
	Newfoundland	0,111	0,0003	0,00002	2,7	0,06	0,00032
	Antilles	0,220	0,029	0,004	131,8	0,14	0,033
	Remaining islands	0,040	0,001	0,00006	25,0	0,06	0,00106
	Total	9,210	0,494	0,039	53,6	0,08	0,533
Pacific	Continent	4,800	2,186	0,481	455,4	0,22	2,667
	Islands	0,151	0,071	0,016	470,2	0,22	0,086
	Total	4,951	2,257	0,496	455,9	0,22	2,753
Global		23,401	2,833	0,544	121,1	0,19	3,377

TABLE 5. Solid River Runoff into the Global Ocean from the Territory of South America

Basin	Sector	Drainage area, 10 ⁶ km ²	Suspended loads, 10 ⁹ tons/yr	Traction loads, 10 ⁹ tons/yr	Av. modulus of sus- pended load runoff, 10 tons/km ² yr	Ratio of traction loads to suspended loads	Total solid runoff, 10 ⁹ tons/yr
Atlantic	Basins of the Amazon, Uruguay, and Parana rivers	8,992	0,609	0,097	67,7	0,16	0,706
	Remaining territory	6,086	0,670	0,108	110,1	0,16	0,777
	Tierra del Fuego Archipelago	0,072	0,006	0,001	83,3	0,16	0,007
	Total	15,150	1,285	0,206	84,8	0,16	1,491
Pacific	Continent	1,240	0,565	0,124	455,6	0,22	0,689
Global		16,390	1,850	0,330	112,9	0,18	2,180

TABLE 6. Solid River Runoff into the Global Ocean from the Territory of Australia

Basin	Sector	Drainage area, 10 ⁶ km ²	Suspended loads, 10 ⁹ tons/yr	Traction loads, 10 ⁹ tons/yr	Av. modulus of sus- pended load runoff, 10 ³ tons/km ² yr	Ratio of traction loads to suspended loads	Total solid runoff, 10 ⁹ tons/yr
Pacific	Continent	0,613	0,014	0,003	22,8	0,22	0,017
	New Zealand	0,265	0,267	0,059	1007,5	0,22	0,326
	New Guinea and Tasmania	0,843	0,019	0,004	22,5	0,22	0,024
	Total	1,721	0,301	0,066	174,9	0,22	0,367
Indian	Northern Australia	1,170	0,328	0,020	280,3	0,06	0,348
	Southern Australia	1,908	0,057	0,009	29,9	0,16	0,066
	Tasmania	0,180	0,050	0,003	277,8	0,06	0,053
	Total	0,047	0,001	0,0002	21,3	0,16	0,002
Global		3,305	0,437	0,032	132,2	0,07	0,469
		5,026	0,738	0,098	146,8	0,13	0,836

In the calculations performed by the author reliable determinations of the average multi-layer runoff of loads for 436 rivers were utilized (the period of observations was as a rule no less than 10 years). The observations were conducted at the river mouths or in their immediate proximity [3]. The distribution of the studied river basins over oceanic drainage areas: in the Arctic: 35 river basins (66% of the total drainage area of the ocean); in the Atlantic: 255 (69%); in the Pacific: 128 (43%); in the Indian 18 (43%).

For the determination of solid river runoff from every oceanic drainage area, the calculation was carried out differentially, by sectors (the method of local extrapolation). For this, a series of sectors was distinguished in the limits of each oceanic drainage area. These sectors were characterized by close values of the modulus of suspended load runoff for the studied river basins and by similar landscape-climatic-geomorphologic conditions, and degree of Quaternary alternation of natural landscapes, that is, by the factors that significantly influence the intensity of river erosion (Fig. 1). The differential approach to the determination of solid runoff of river loads permits a comparative decrease in errors which may arise in the calculation of loads from the uneven distribution of drainage area observation stations in the global extrapolation method.

The areas of the distinguished sectors were calculated by the template method on maps at a scale of 1:30,000,000. The boundaries and areas of oceanic drainage basins were taken from [6].

Ratios of drag loads to suspended loads were used for the calculation of traction load runoff. Their average values may be taken as 0.06 for level rivers (data from 111 points of observation), 0.16 for level rivers with mountain sources (from 24 points), 0.22 for low and intermediate mountain rivers (87 and 58 points respectively), and 0.29 for high mountain rivers (from 13 points) [3].

The distribution of solid runoff from the drainage area sectors distinguished within the limits of each continent is presented in Tables 1-6. The quantity of suspended and traction loads entering the oceans from the different continents is presented in Table 7, while Table 8 shows the new estimate of solid river runoff into the global ocean and for comparison previous estimates which were performed by A. P. Lisitsyn [4].

The total solid runoff of rivers into the global ocean comes to $19.288 \cdot 10^9$ tons/yr. Of that number, $16.303 \cdot 10^9$ tons/yr (85%) is suspended load, and $2.985 \cdot 10^9$ tons/yr (15%) is traction load. As we see the traction loads neglected earlier are approximately comparable to the total quantity of sedimentary material of glacial and eolian supply (1.5 and $1.6 \cdot 10^9$ tons/yr, respectively [4]). The new estimate of suspended load runoff into the global ocean is $2.2 \cdot 10^9$ tons/yr less than the estimate of A. P. Lisitsyn [4]. The suspended runoff into the Indian ocean was shown to be particularly increased over previous calculations, by more than $3 \cdot 10^9$ tons/yr, while comparatively close values are obtained for the Atlantic, Arctic, and Pacific oceans. Regardless that different values for the areas of oceanic drainage basins were used in the calculations, the differences in the estimates are primarily connected with differences in the methods of their acquisition, which is easily convincing by calculating the relative runoff (average moduli of suspended load runoff) from the new and old data.

The significant disagreement in estimates of solid runoff into the Indian ocean is connected with the fact that in previous calculations 62% of the considered areas occurred on rivers that were anomalous in their quantity of solid runoff for the respective landscape-climatic zones (Ganges, Brahmaputra, Irrawaddy, Indus, Tigris, and Euphrates), which make up only 24% of the total Indian ocean drainage area of Asia. This anomaly was closely connected with the significantly higher degree of Quaternary alteration within the basin limits of the named rivers in comparison with other regions of the Indian ocean drainage area [1-3]. Naturally, mechanical extrapolation of data from the anomalous rivers over the remaining 76% of the drainage area territory led to a significant increase in the total estimate of suspended load runoff into the Indian ocean.

The insignificant understatement (by $0.7 \cdot 10^9$ tons/yr) of solid river runoff into the Atlantic and Arctic oceans in the previous estimate is apparently connected with the fact that data were disregarded on the mountain rivers of the Balkans, Apennines, Pyrenees Peninsula, Atlas, Asia Minor, and Caucasus (4% of the total drainage area of the two oceans). The moduli of solid runoff for these neglected territories ($500-1500$ tons/km² yr) significantly exceed the moduli of suspended load runoff of level rivers (as a rule, less than 100 tons/km² yr), which A. P. Lisitsyn [4] primarily used in his derivation of the total suspended load runoff into the Atlantic and Arctic oceans.

TABLE 7. Solid River Runoff into the Global Ocean from the Continents

Basin	Sector	Drainage area, 10 ⁶ km ²	Suspended loads, 10 ⁹ tons/yr	Traction loads, 10 ⁹ tons/yr	Av. modulus of suspended load runoff, 10 ⁹ tons/km ² yr	Ratio of trac- tion loads to sus- pended loads	Total solid run- off, 10 ⁹ tons/yr
Arctic	Europe	1,531	0,013	0,0008	8,5	0,06	0,014
	Asia	11,672	0,107	0,013	9,2	0,12	0,120
	North America	9,240	0,082	0,009	8,9	0,11	0,091
	Total	22,443	0,202	0,023	9,0	0,11	0,225
Atlantic	Europe	6,769	0,974	0,205	143,9	0,21	1,179
	Asia	0,627	0,231	0,051	368,4	0,22	0,282
	Africa	14,930	0,685	0,111	45,9	0,16	0,796
	North America	9,210	0,494	0,039	53,6	0,08	0,533
	South America	15,150	1,285	0,206	84,8	0,16	1,491
	Total	46,686	3,669	0,612	78,6	0,17	4,281
Pacific	Asia	11,905	4,237	0,750	355,9	0,18	4,987
	North America	4,951	2,257	0,496	455,9	0,22	2,753
	South America	1,240	0,565	0,124	455,6	0,22	0,689
	Australia	1,721	0,301	0,066	174,9	0,22	0,367
	Total	19,817	7,360	1,436	371,4	0,20	8,796
Indian	Asia	6,996	4,194	0,811	281,1	0,19	5,005
	Africa	5,610	0,441	0,071	78,6	0,16	0,512
	Australia	3,305	0,437	0,032	132,2	0,07	0,469
	Total	15,911	5,072	0,914	318,8	0,18	5,986
Global	Europe	8,300	0,987	0,206	118,9	0,21	1,193
	Asia	31,200	8,769	1,625	281,1	0,19	10,394
	Africa	20,540	1,126	0,182	54,8	0,16	1,308
	North America	23,401	2,833	0,544	121,1	0,19	3,377
	South America	16,390	1,850	0,330	112,9	0,18	2,180
	Australia	5,026	0,738	0,098	146,8	0,13	0,836
	Total	104,857	16,303	2,985	155,5	0,18	19,288

TABLE 8. Solid River Runoff into the Global Ocean

Ocean	Drainage area with- out An- tarcica, 10 ⁶ km ²	Considered data on suspended runoff		Calculated data on solid run- off, 10 ⁹ tons/yr		
		drainage area, 10 ⁶ km ²	suspended loads, 10 ⁹ tons/yr	suspended loads	traction loads	total solid runoff
Arctic	22,443 (67,36)*	14,727 (41,17)*	0,135 (1,95)*	0,202 (3,191)*	0,023 —	0,225 —
Atlantic	46,686	31,996	1,753	3,669	0,612	4,281
Pacific	19,817 (18,13)	8,510 (7,61)	3,504 (2,98)	7,360 (7,152)	1,436 —	8,796 —
Indian	15,911 (17,21)	6,791 (6,77)	3,190 (3,15)	5,072 (8,186)	0,914 —	5,986 —
Total	104,857 (102,70)	62,024 (55,55)	8,582 (8,08)	16,303 (18,529)	2,985 —	19,288 —

*Total value for Arctic and Atlantic oceans. A. P. Lisitsyn's data [4] are given in parentheses.

Estimates of suspended river runoff into the Pacific ocean somewhat unexpectedly appeared practically identical (a discrepancy of only $0.2 \cdot 10^9$ tons/yr towards a decrease of the previous estimate). However, the analysis used in the calculation of the data shows that this coincidence is chance. In fact, in the previous calculation, nearly 50% of the area of the considered river basins occur on rivers of Southeast Asia (Huang He, Yangtze, Mekong, Khongkha) which are characterized by high moduli of suspended load runoff. At the same time, the basins of these rivers occupy nearly 20% of the area within the limits of the entire drainage area. As a result, the average modulus of suspended load runoff which was calculated for the considered territory and extrapolated over the entire drainage basin was shown to be comparatively high — 392 tons/km² yr, but less than the average moduli of solid runoff for the mountainous drainage areas of North and South America (31% of the total area of the Pacific ocean drainage area), which are obtained based on the appearance of new data (see Fig. 1). The relative average runoff of such anomalous regions as the basins of the Huang He and Khongkha rivers and the

island of New Zealand was simultaneously shown to be still more decreased in the calculation of the derived average modulus. However, in the resultant estimate, the decrease of runoff in the considered regions was almost completely compensated by its significant increase in the Asiatic drainage area of the more northern Huang He river and in Australia, for which average moduli of suspended load runoff are calculated for actual data of hydrological stations (see Fig. 1). It is easy to be convinced that such compensation is random by carrying out the corresponding calculations.

The new estimate of solid river runoff including traction and suspended loads, makes it possible to obtain a conception of the quantity of detrital material of different granulometric types entering the ocean. There are quite valid data in agreement with which the average median diameter of the of the suspended loads varies from 0.045 to 0.058 mm (results of granulometric analysis of suspended matter from 596 rivers of various landscape-climate zones), while the traction loads vary from 0.49 to 32.1 mm (295) [3]. On the basis of these data, disregarding the comparatively poor sorting of river loads, it is possible to draw the conclusion that the primary mass of the suspended loads is represented by silty-pelitic material ($M_d < 0.1$ mm), while the traction loads are represented by sandy and coarser grained material. Thus, rivers annually put $16.3 \cdot 10^9$ tons of silty-pelitic and $3 \cdot 10^9$ tons of sand-gravel-pebble sedimentary material into the global ocean.

Considering that in the applied methodology, the discrimination of the sectors of oceanic drainage areas was made on the basis of similarity in the factors which affect the characteristics of the solid river runoff, and that each sector is characterized to one degree or another by actual determinations of solid runoff, there is every reason to assume that the calculated estimate of solid runoff is close to the actual amount, and that it will not significantly vary with the appearance of new data on unstudied regions. To a significantly larger degree it is necessary to anticipate variations in the quantity of solid river runoff into the global ocean due to the further increase of anthropogenic influences on rivers and their drainage territories. However, the elucidation of this aspect is beyond the bounds of the present article. It is necessary to note here that the new estimate of suspended load runoff ($16.3 \cdot 10^9$ tons/yr) is insignificantly distinguished from the estimate of V. V. Alekseev and K. N. Lisitsyn ($15.7 \cdot 10^9$ tons/yr [6]) which was calculated by a similar method based on a smaller volume of factual material, which, judging by the publications of the last decade remains beyond the field of knowledge of specialists who are studying contemporary sedimentogenesis in seas and oceans.

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CONSTITUTION AND GEOCHEMISTRY OF THE SUSPENDED MATTER
OF THE TEREK RIVER

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This paper characterizes the composition of the suspended matter for the upper, middle, and lower reaches of the Terek River. The topography, climate, and rock composition of catchment areas have been found to determine mainly the amounts of the suspended matter carried by the Terek and its carbonate content. The granulometry of suspensions is affected less by physical geography. The mineral and chemical compositions of the carbonate-free component of solid discharge remains virtually the same from the source to the mouth. Depending on the amount of suspended matter carried by the river, only the absolute weights of the elements in the solid discharge have been observed to fluctuate.

Studies of the formation of solid river discharge are essential, because it is the main source of sediments in seas and oceans, and most of the elements are carried into basins in a suspended form [2, 5-7, 9-12, 14, 20-24].

Strakhov (1954) described in general terms how the mobilization and transport of material on continental surfaces are affected by the physical-geographic environment and especially the topography, climate, and rock petrography. For detailed descriptions of the material transport by rivers, basins of individual rivers should be studied as well as larger areas. Little data have been accumulated so far, however, on the variations along the course of large rivers.

Isolated studies [8, 13, 25] have reported fluctuations in water turbidity and suspension granulometry along a river course. The migration of elements in river water has been studied mainly in estuarine parts of rivers [5, 7, 11, 12, 14, 24].

The present paper characterizes the composition of suspended matter in the upper, middle, and lower reaches of the Terek River. The study included granulometric, mineralogic, and chemical investigations of suspensions.

METHODS

Samples of high tide Terek waters were collected by the author together with D. S. Turovskii in August of 1981. The samples were taken midstream from a depth of 0.3-0.5 m with polyethylene canisters. Eleven samples were collected from the upper reaches downstream: at the upper reaches of the river near Kobi Village, in Dar'yal Gorge, and near Balta Village; in the middle reaches, 2 km upstream of El'khotovo and near Ishcherskaya; and at the lower reaches, near Kargalinskaya, 5 km (Damba) and 1 km from the river mouth (Ust'e).

The suspended matter and solution in specimens were separated by free or vacuum filtration through Sinpor membrane ultrafilters with a pore size of 0.17 μm .

The fractions of suspended matter (<0.001 ; $0.001-0.01$; >0.01 mm) were separated by roiling. By the method of suites, the fraction of >0.01 mm was divided into $0.01-0.1$; $0.1-1.0$; >1.0 mm; the heavy and light subfractions were then divided in bromoform.

The mineralogic investigation of pelitic (<0.001 , $0.001-0.01$ mm) fractions of the suspended matter was conducted by diffractometry. The siltstone ($0.01-0.1$ mm) and sand fractions ($0.1-1.0$; >1.0 mm) were investigated microscopically.

The amounts of Si, Al, Ti, Fe, Mn, Ca, Mg, P, Na, K, CO_2 , C_{org} in suspension were determined by chemical techniques; Cr, V, Ni, Co, Cu, Mo, Ga, Ge, and Pb by quantitative spectral

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analysis, and Zn, Zr, Ba, Sr by the x-ray fluorescence method. All the analyses were performed in the laboratories of the Geological Institute of the USSR Academy of Sciences.

GENERAL PHYSICAL-GEOGRAPHICAL DESCRIPTION OF THE TEREK RIVER BASIN

The Terek is the largest and most powerful water stream of the western shore of the Caspian Sea. Its total catchment area is 43,710 km², it is 591 km long, and it has a multiannual average flow of 9.7 billion m³ with 25.3 billion tons of suspended matter and 3.09 billion tons of dissolved matter [4, 13]. The basin of the Terek exhibits a broad diversity of natural environments [1, 13, 15-19, 25].

The Terek flows through mountainous, piedmont, and plainland Northern Caucasus. At its upper reaches, it is a typical mountain river with numerous subsidiaries and a grade of 15-5%. From its springs to Balta, near the Greater Caucasus, Bokovoy, and Skalistyi ridges, the Terek flows in narrow gorges with a rocky bed, shallows, and rapids. In the middle course from El'-khotovo to Ishcherskaya the river emerges onto the Stavropol plateau and the Tersk-Kuma plain. The grades decrease to 5-1%, the river valley expands, there appear islands, sandbanks, and shoals, and there are fewer subsidiaries. At the lower reaches, the grade declines to 1-0.1% and the riverbed expands to 500-1000 m, and begins to meander between low easily erodible banks. Near the river mouth downstream from Kargalinskaya, the Terek forms a gigantic delta of 4000 km². The river divides into channels with estuarine sandbars and numerous shallow lakes (bayous) between them.

The topographic pattern determines the climatic zonality of the Terek River basin. In mountainous areas with cold and moist climates, the annual average air temperature is -4°C; the total annual precipitation is on average 700 mm/yr. In the piedmont areas, with a temperate climate, the annual average temperature is +8.6°C; the precipitation is 600 mm/yr. On the plane, with its arid and hot climate, the annual average temperature is +9.6°C; the total precipitation drops to 400-450 mm/yr, with an evaporation rate of 650 mm/yr, i.e., 1.5 times more than the annual precipitation.

Rocks of various age and composition are found on catchment areas. From the springs to the Kobi the Terek flows through Upper Jurassic carbonate rocks. Further down, it erodes Lower Jurassic terrigenous strata. Near Kazbegi the Terek drains Upper Pliocene effusives and Early and Middle Quaternary volcanogenic formations (andesite, andesite-dacite, dacite, and rhyolite). In the Dar'yal gorge the river erodes Paleozoic granite; from the Verkhniy Lars to Balta it flows through Lower/Middle Jurassic and Middle Quaternary terrigenous sediments. North of Balta, Upper Jurassic and Lower Cretaceous carbonate rocks and Middle/Upper Quaternary sand-clay sediments are common. Near Ordzhonikidze the Terek Valley cuts across low Pastbishchnyi ridge mountains, formed of Upper Cretaceous limestone, marlstone, and sandstone and Paleogene/Neogene terrigenous and carbonate rocks. From Ordzhonikidze to Sunzha ridge the Terek flows over Recent and Upper Quaternary sand-clay sediments. The Sunzha ridge consists of sand and clay beds with Lower/Middle Neogene marl interlayers.

At the middle and lower reaches, the Terek erodes Quaternary rocks consists of dense alluvial-diluvial-proluvial loesslike loam, river sand, and clay. The Recent stage is represented by flood plain and first terrace sediments. At the middle of its course, from El'-khotovo to Ishcherskaya, alluvial sediments are predominant; they gradually give way to alluvial-diluvial rocks. At the lower reaches, starting from Kargalinskaya, the Terek drains alluvial-marine, lacustrine-fluvial, and aeolian sediments.

The lithologic-geomorphologic and climatic variety of the Terek basin is responsible for a broad spectrum of soils and plant covers on this territory. At the upper reaches of the river, at altitudes of 2000-2500 m, brown mountain meadow soils with subalpine, alpine, and subnival belt vegetation are common. At the middle reaches, in the piedmont, black chernozem with tipchak-meadow grass and diverse grass and serial vegetation are observed. Brown soils with a heightened content of gypsum and water-soluble salts are common on the ancient Quaternary terraces. In the delta are meadow-chestnut, meadow-marsh, peat bog-swamp, and ooze-swamp soils with solonchaks, characterized by a heightened content of highly soluble salts. Water swamp vegetation with reeds is typical for the Terek delta.

The alimentation sources of the Terek are diverse. They include thaw water from glaciers and snow, atmospheric precipitation, and, to a lesser degree, groundwater. At the upper and middle reaches, the river is fed by glacial water more than at the lower reaches. Atmospheric precipitation is of a subordinate importance for the lower reaches. The water flow peaks in July and August and is at its lowest point in the winter.

TABLE 1. Mechanical Composition of Suspended Matter in the Terek River

Part of the river	Specimen collection site	Specimen number	Turbidity, g/liter	Yield of fractions, % (fraction, mm)				
				<0.001	0.001—0.01	0.01—0.1	0.1—1.0	>1.0
Upper reaches	Kobi	1b	10.125	17	36	45	1	1
		2b	17,500	14	37	45,5	2	1,5
	Balta	3b	30,70	14	45	40	0.6	0.4
Middle reaches	El'khotovo	4b	0.85	26,7	39	30,3	2,0	2,0
	Ishcherskaya	6b	0.75	36,9	18,5	40,7	2,3	1,6
Lower reaches	Kargalinskaya	7b	0.90	20,0	30,0	46,7	2,0	1,3
	Damba	9b	1.19	22,0	41,2	36,6	0.8	0.4
	Ust'e	10b	1.21	33,3	41,7	25,0	Fraction absent	

Chemically, the Terek waters are mainly of the hydrocarbonate-calcium type, although closer to the river mouth the water acquires a sulfate-calcium character.

From the upper reaches to the river mouth the terrain exhibits a broad variety: the topography changes drastically (from the high mountains of the Greater Caucasus to the North Dagestan lowlands); the climate varies intensely (from typically humid to pronounced arid); the composition of the rocks in the catchment areas changes contrastively (from Paleozoic granite to Jurassic carbonate and terrigenous rocks to Recent alluvial sediments); and the soil profile and vegetable cover change. All these factors must have had a strong influence on the composition of the river discharge.

GRANULOMETRIC, MINERAL, AND CHEMICAL COMPOSITION OF SUSPENDED MATTER

The physical-geographical features of the Terek basin are reflected primarily in the amount of suspended matter carried by the river: from the upper reaches to the river mouth the turbidity is decreased by a factor of 8-25 (Table 1; Fig. 1a).

In mountain areas, steep slopes, torrential rains, and large amounts of snow thaw water during high tide result in vigorous mechanical erosion; the large riverbed gradient and the tremendous speed of the stream determine its transport capacities. Hardly any of the material carried by the river is deposited in the riverbed; during high tide and flood seasons it is carried downstream. As a result, the highest turbidity is observed at the upper reaches. According to our data, suspended matter near Kobi amounts to 10.125 g/liter; in Dar'yal gorge it rises to 17.500 g/liter, and near Balta, where easily erodable Middle and Upper Quaternary sediments are widespread, in catchment areas the turbidity rises to 30.682 g/liter.

The mechanical washdown from catchment areas in the piedmont part is much smaller, mainly because of lower slope gradients and reduced amounts of precipitation. The riverbed slope is much smaller here and the flow is slower; some of the suspended particles become deposited on the bottom, and alluvial sediments accumulate in some locations in the river valley. The quantity of suspended matter at the middle reaches of the river is greatly reduced. Near El'khotovo the turbidity is 0.85 g/liter; near Ishcherskaya 0.75 g/liter.

The plain region, with hot and arid climate, is a territory with minute mechanical erosion. The amount and level of water in the river are reduced, the flow slows down, and the suspended material becomes deposited actively, with intense sediment accumulation in the river valley. A slight increase in turbidity at the lower reaches is caused by the erosion of loose alluvial sediments and the high evaporation rate that exceeds the annual atmospheric precipitation. At Kargalinskaya the river carries 0.900 g/liter of suspended matter, at Damba 1.19 g/liter, and at Ust'e 1.21 g/liter.

Offtake into irrigation systems slightly modifies the true turbidity in the estuarine area: the rapid drop of water level in the river combined with a high speed of the stream results in an increased amount of material carried due to the roiling of riverbed sediments.

Depending on the topography, climate, and rock formations of catchment areas, the river's regime and its transporting force are varied, which is reflected in the amount of material the river carries, i.e., in its turbidity. However, there is no direct correlation between the

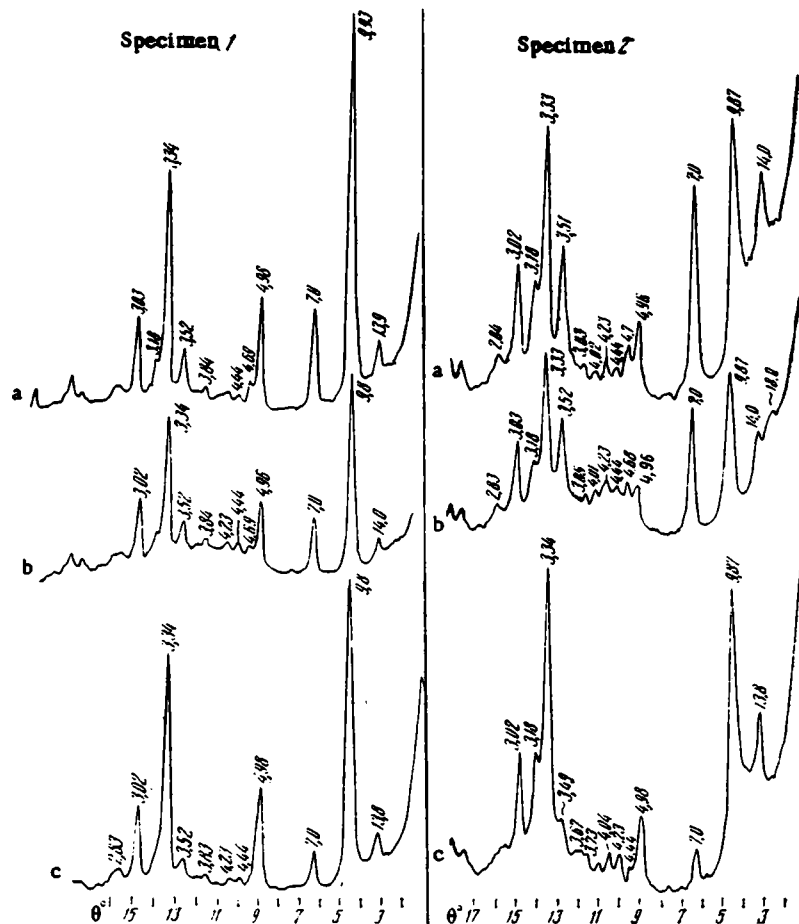


Fig. 1. Diffractograms of the clay fraction <0.001 mm of suspended matter at the upper reaches (specimen 1, Kobi) and the lower reaches (specimen 2, Damba) of the Terek River. Specimens: (a) natural, (b) glycerine-treated, (c) heated at 550°C .

granulometric composition and total turbidity (see Table 1). Along the entire river, for example, the main fractions in Terek suspensions are the silt fractions (0.01–0.1 mm) and the coarse-pelitic fraction (0.001–0.01 mm), accounting for 25–48% (mean 39%) and 18–45% (mean 36%), respectively. The fine pelitic fraction (<0.001 mm) ranges from 14 to 37% (mean 23%). Sand fractions (0.1–1.0 mm) vary from 0 to 4% (mean 2.5%). Downstream from the upper reaches to the river mouth, however, there is a tendency for the suspended matter to become finer; at the mouth the sum of the pelitic fractions rises to 75%. The proportion of the heavy sub-fraction in the silt and sand fractions is virtually the same along the river course, ranging from traces to 0.01%.

A homogeneous mineralogic composition is a typical trait of Terek's suspended matter (Table 2). The pelitic fractions (<0.001 ; 0.001–0.01 mm) contain hydromica, chlorite, quartz, calcite, feldspar, traces of smectite, and cristobalite. The silt (0.01–0.1 mm) and sand fractions (0.1–1.0 mm) contain fragments of terrigenous and carbonate rocks, quartz, feldspar, carbonate grains, iron hydroxide grains, and mica. The main minerals of the heavy fraction are pyroxenes; iron sulfide, hornblende, and grains of garnet, zircon, sphene, and staurolite are also found.

The differences of mineralogic composition between the parts of the river course are limited to minor variations in the sets of minerals and variable proportions of components as well as carbonate contents.

The main chemical composition of Terek suspensions varies noticeably only in the carbonate content (Table 3). Specimen 1b, from the upper reaches of the river (Kobi), is remarkable; the carbonate content rises to 13.7% CO_2 , while the contents of the other elements except for

TABLE 2. Mineral Composition of Suspended Matter in the Terek River

Part of the river	Specimen collection	Specimen number	Fraction, mm			
			< 0.001	0.001-0.01	0.01-0.1	0.1-1.0
Upper reaches	Kobi	1b	Al-hydromica, chlorite, calcite	Al-hydromica, chlorite, quartz, calcite, feldspar, sometimes, cristobalite	Mainly carbonates—carbonate fragments and aragonites (needles), minor amount of small quartz and feldspar fragments; single ore minerals—iron sulfides and hydroxides	Mainly rock fragments of sedimentary (carbonate) rocks, partly ferruginated; some presence of ferruginous carbonates (possibly, siderite); subordinate amount of quartz and altered feldspar
	Dar'yal gorge	2b	Al-hydromica, chlorite, quartz, feldspar, possibly cristobalite	Al-hydromica, chlorite, quartz, feldspar, possibly cristobalite	Mainly rock fragments (heavily altered), subordinate quantities of quartz and feldspars, carbonate grains, rare hydroxides of iron, pyroxene (rhombic and monoclinic), black ore minerals (possibly sulfides), hornblende (ordinary and basaltoid), and staurolite	Rock fragments, mainly sedimentary (clay schists, quartzites, quartz rocks), carbonate grains, ore minerals (sulfides?), and vegetable remains
	Balta	3b	Al-hydromica, chlorite, quartz, feldspar	Al-hydromica, chlorite, quartz, feldspar	Rock fragments (mainly), subordinate amounts of quartz, feldspar carbonate grains, rare iron hydroxides, sulfides, and pyroxenes	Mainly sedimentary rock fragments (schists, possibly coaly), some quartz, rare carbonates
Middle reaches	El'khotovo	4b	Al-hydromica, chlorite, quartz, feldspar, calcite	Hydromica, chlorite, quartz, feldspar	Rock fragments, mainly sedimentary (altered schist), large amounts of quartz, rare hydroxides of iron, sulfides, pyroxene, single grains of garnet, zircon, staurolite, and sphene	Rock fragments, quartz, feldspars, iron hydroxides

Lower reaches	Ishcherskaya	6b	Hydromica, chlorite, quartz, feldspar, traces of smectite and cristobalite	Hydromica, chlorite, quartz, feldspar, gypsum, possibly cristobalite	Equal amounts of rocks and quartz, some carbonates, feldspar, a little mica, iron hydroxide, single grains of garnet, zircon, and sphene	Large amounts of shreds of vegetable organics, mica, rock fragments, and quartz
	Kargalinskaya	7b	Hydromica, chlorite, quartz, feldspar, possibly cristobalite and traces of smectite	Hydromica, chlorite, quartz, feldspar, cristobalite, calcite (?)	Rock fragments and quartz (in equal proportions), carbonates, small amounts of mica and feldspar, rare grains of pyroxene, sphene, and garnet	Large amounts of vegetable organics, some mica and rock fragments
	Damba	9b	Hydromica, chlorite, quartz, feldspar, calcite, traces of smectite	Hydromica, chlorite, quartz, feldspar, calcite, possibly cristobalite	Mainly quartz, less rock fragments (partially ferruginated), abundant mica (muscovite, chlorite), fragments of iron hydroxides, remains of (carbonate) organisms, single grains of heavy fractions, mainly pyroxenes, with some epidote, zircon, hornblende, titanium-containing minerals, and sphene	Mainly fragments of vegetable organics with some rock fragments (sedimentary and carbonate), carbonate fragments, large flakes of chloritic and muscovitic micas
	Ust'e	10b	Hydromica, chlorite, quartz, feldspar, calcite, traces of smectite, possibly cristobalite	Hydromica, chlorite, quartz, feldspar, calcite, traces of smectite, possibly cristobalite	Mainly quartz, less rock fragments, abundant mica (muscovite, chlorite), fragments of iron hydroxides, small amounts of carbonate grains, remains of (carbonate) organisms, single grains of heavy fraction - mainly pyroxenes with some epidote, zircon, hornblende, and titanium-containing minerals	Same

TABLE 3. Main Chemical Composition of Suspended Matter from the Terek River, %

Part of the river	Specimen collection site	Specimen number	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	H ₂ O+	H ₂ O-	CO ₂	C _{org}	Annealing loss
Upper	Kobi Dar'yal gorge Balta	1b	41,63	0,51	14,63	2,10	1,67	0,09	1,41	19,25	1,43	2,38	0,20	2,91	0,24	13,70	0,53	—
		2b	57,56	0,99	17,48	4,59	3,29	0,18	2,93	2,61	2,25	2,80	0,20	3,65	0,64	0,40	0,11	—
		3b	55,87	0,68	18,71	4,33	3,23	0,18	2,16	2,54	1,69	2,93	0,22	3,86	0,62	None	0,63	2,16
Middle	El'khotovo Ishcherskaya	4b	55,67	0,96	16,60	1,38	4,20	0,17	2,89	4,75	1,92	2,80	0,18	3,74	0,78	2,60	0,91	—
		6b	55,34	0,90	14,59	3,74	2,65	0,12	2,65	6,11	1,99	2,62	0,19	2,64	1,38	4,25	0,51	—
Lower	Kargalinskaya Damba Ust'e	7b	55,64	0,72	14,79	3,86	2,05	0,12	2,01	6,47	1,85	2,44	0,21	1,10	3,02	2,85	0,58	—
		9b	53,02	0,99	14,50	3,59	2,52	0,12	2,67	6,62	1,69	2,80	0,17	3,46	1,75	4,40	1,36	—
		10b	53,76	0,72	14,83	4,17	1,79	0,10	1,99	7,23	1,78	2,44	0,18	1,34	3,42	1,85	0,32	—
Av. for Terek			53,56	0,81	15,39	3,47	2,68	0,14	2,34	6,95	1,82	2,65	0,19	2,84	1,48	3,76	0,62	—
Av. for world rivers [6]			54,80	0,67	15,65	7,28	Not det'd	0,14	2,07	3,52	1,35	1,82	0,14	Not det'd	Not det'd	Not det'd	Not det'd	—

TABLE 4. Contents of the Chemical Elements in Suspended Matter of the Terek River (recalculated to carbonate-free matter)

Part of the river	Specimen collection site	Specimen No.	Si	Ti	Al	Fe	Mn	Mg	Na	K	P	Cr	Ni	V	Cu	Co	Pb	Ga	Ge	Mo	Zn	Zr	Sr	Ba
Upper	Kobi Dar'yal gorge Balta	1b	28,22	0,30	8,92	4,00	0,10	1,23	0,77	1,44	0,13	80	44	97	49	17	20	17	2,2	2,2	72	203	914	392
		2b	26,90	0,40	9,25	5,77	0,14	1,77	0,83	1,16	0,09	72	48	118	54	26	36	26	1,5	1,5	n.d.	n.d.	n.d.	n.d.
		3b	26,11	0,28	9,90	5,54	0,14	1,30	0,63	1,22	0,10	74	50	112	62	32	36	26	1,5	1,5	200	340	200	470
Middle	El'khotovo Ishcherskaya	4b	27,58	0,41	9,31	4,48	0,14	1,84	0,75	1,23	0,08	69	42	108	57	17	228	23	1,6	1,6	498	297	276	466
		6b	28,70	0,41	8,57	5,18	0,10	1,78	0,82	1,21	0,09	73	40	98	59	18	86	24	2,2	3,8	388	278	311	477
Lower	Kargalinskaya Damba Ust'e	7b	27,82	0,31	8,38	4,59	0,10	1,30	0,74	1,08	0,10	79	38	104	52	15	70	24	1,6	3,0	268	272	310	471
		9b	27,51	0,44	8,51	4,96	0,10	1,79	0,70	1,29	0,08	74	40	108	58	18	70	24	1,7	3,6	266	233	311	477
		10b	26,13	0,30	8,16	4,47	0,08	1,25	0,69	1,05	0,08	73	37	96	51	14	67	25	1,6	3,3	239	270	326	468
Av. for Terek			27,37	0,36	8,88	4,87	0,11	1,53	0,74	1,21	0,09	74	42	105	55	20	77	24	1,7	2,6	276	270	378	460
Av. for world rivers [6]			25,61	0,4 ± 0,1	8,28	5,1 ± 1,40	0,11 ± 0,05	1,25	1,00	1,50	0,06	130 ± 52	84 ± 25	126 ± 32	80 ± 30	18 ± 10	47 ± 50	18 ± 4	n.d.	5,8	300 ± 70	200 ± 40	270 ± 90	380 ± 160

Note: The contents of Si, Ti, Al, Fe, Mn, Mg, Na, K, and P are in percentages; for the other elements the contents are indicated as $\text{n} \cdot 10^{-4} \%$; n.d., not determined.

TABLE 5. Absolute Quantities of Chemical Elements

Part of the river	Specimen collection site	Specimen No.	Turbidity g/liter	Si	Ti	Al	Fe	Mn	Ca	Mg	Na	K	P	Cr
Upper	Kobi Dar'yal gorge	1b	10,12	2857,28	30,38	903,15	405,00	10,12	2019,94	124,54	77,96	145,80	13,16	810,0
		2b	17,50	4707,50	70,00	1618,75	1009,75	24,50	325,50	309,75	145,25	203,00	15,75	1260,0
	Balta	3b	30,70	8015,77	85,96	3039,30	1700,78	42,98	558,74	399,10	193,41	374,54	30,70	2271,8
Middle	El'khotovo	4b	0,85	234,43	3,48	79,14	38,08	1,19	30,60	15,64	6,38	10,46	0,68	58,55
	Ischerskaya	6b	0,75	215,25	3,08	64,27	38,85	0,75	36,38	13,35	6,15	9,08	0,68	54,75
Lower	Kargalinskaya	7b	0,90	250,38	2,79	75,42	41,31	0,90	44,46	11,88	6,66	10,49	0,90	71,1
	Damba	9b	1,19	327,37	5,24	101,27	59,00	1,19	62,48	21,30	8,33	15,35	0,95	88,1
	Ust'e	10b	1,21	316,17	3,63	98,74	58,32	0,97	65,10	15,12	8,35	13,67	0,97	88,3

Part of the river	Specimen collection site	Specimen No.	Turbidity g/liter	Ni	V	Cu	Co	Pb	Ga	Ge	Mo	Zn	Zr	Sr	Ba
Upper	Kobi Dar'yal gorge	1b	10,12	445,5	982,1	495,1	172,1	202,5	172,1	22,3	22,3	728,6	2055,4	9254,2	3630,0
		2b	17,50	840,0	2065,0	945,0	455,0	630,0	455,0	26,2	26,2	n.d.	n.d.	n.d.	n.d.
	Balta	3b	30,70	1473,6	3438,4	1903,4	982,4	1105,0	798,2	46,0	46,0	6140	10438	6140,0	14420
Middle	El'khotovo	4b	0,85	35,7	91,8	48,45	14,4	193,8	19,5	1,4	1,4	423,3	252,4	234,6	396,1
	Ischerskaya	6b	0,75	30,0	73,5	45,0	13,5	65,25	18,0	1,8	2,9	291,0	208,5	233,2	357,8
Lower	Kargalinskaya	7b	0,90	34,2	93,6	46,8	13,5	63,0	21,6	1,4	2,7	241,2	244,8	279,0	423,9
	Damba	9b	1,19	47,6	128,5	69,0	21,4	83,3	28,6	2,0	4,3	316,5	277,3	370,1	567,6
	Ust'e	10b	1,21	44,8	116,2	61,7	16,9	81,1	30,2	1,9	4,0	289,2	326,7	394,5	566,3

Note: The contents of Si, Ti, Al, Fe, Mn, Ca, Mg, Na, K and P are in mg/liter; other elements in g/liter; n.d., not determined.

Sr are lowered. The high CO₂ concentration in this specimen can be linked to the erosion of Upper Jurassic carbonate rocks: the sum of the siltstone and sandstone fractions is 47%. The main constituent of these fractions is carbonate rock fragments; in pelitic fractions, significant amounts of calcite are present. Due to the high carbonate content, Sr concentration in the suspended matter near Kobi is increased by almost 2.5 times. In terms of carbonate-free matter, both rock-forming main elements and trace elements are contained in Terek suspensions along the entire river course in practically equal proportions, which are quite close to the mean contents for suspended matter in the rivers of the world (Table 4), i.e., the granulometry and mineralogy and, therefore, the petrographic features of the rocks being eroded are not reflected in the chemical composition of suspensions to any substantial degree.

The absolute amounts of the elements carried by the river in a suspended state decline significantly along the main stream (Table 5). The highest weights of the elements are observed at the upper reaches, where the water turbidity is greatest; in the river mouth a general decline of the total suspended matter is associated with the lowest absolute weights of all the chemical elements in the solid phase.

Abnormally high contents of Pb ($228 \cdot 10^{-6}\%$) in the suspension of specimen 4b (El'khotovo) and Zn ($200-488 \cdot 10^{-6}\%$) virtually along the entire course of the river are attributable to the technogenic pollution of the Terek. The main sources of pollution are the cities of Ordzhonikidze and Mozdok and the waters from the tributaries Ardon (Mazur Concentration Mill), Shelun (Nal'chik), Sunzha (Groznyi), Baksan (Tyrnyauz), and Malka (Prokhladnyi). At the present time, it is impossible to estimate the true Pb and Zn concentrations in Terek suspensions downstream of Ordzhonikidze.

* * *

In conclusion, it should be noted that topography, climate, and composition of rocks of catchment areas affect mainly the amount of suspended matter carried by the Terek and the carbonate content of that matter. The variations of the physical-geographical conditions affect the granulometry of suspensions much less. The mineral and chemical composition of the carbonate-free component of the solid discharge remains virtually unchanged from the source to the mouth. Our data are thus consistent with Strakhov's conclusion that "in the main branches of large river arteries the variegated original eroded matter becomes mixed and leveled, producing, so to speak, 'average samples' of suspensions" [20].

Due to the shallow depth and the rapid flow of the Terek, at large altitude gradients, suspended matter is mixed intensely and its composition becomes homogenized. The mineral and chemical composition of Terek's suspended matter are formed largely at the upper reaches, where huge amounts of material are washed down from the catchment areas. At the middle and lower reaches the amount of new portions from catchment areas is reduced drastically because of the much slower erosional processes, and they no longer substantially affect the characteristics of suspensions; there is thus no differentiation of suspended matter during the course of its transport, and the river averages its composition. Depending on the amount of material carried by the river, only the absolute weights of elements in the solid discharge are varied.

The variations of the amount and grain size of suspended matter with respect to river depth and its transverse cross section were not taken into account during the sampling. Further studies are expected to add detail to our description of Terek's suspended matter; in particular, it may be possible to describe seasonal and annual fluctuations of its composition.

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Results of rare-earth element (REE) distribution patterns in hydrothermal Fe-Mn-bearing sediments of the ocean are presented. Iron hydroxides are the basic carriers of REE. In the iron silicate-bearing sedimentary-hydrothermal deposits (smectites and nontronites) the REE concentration is an order of magnitude lower than in the hydroxides. The REE-content is due to lithogenic and probably basaltic Al-silicate admixtures. In hydrothermal oxides and silicate-bearing sediments their composition is similar to that of deep ocean waters, with REE admixtures, related terrigenous and basaltic components.

The conduct of rare-earth elements (REE) in the formation of Fe-Mn concretions (FMC) and crusts of hydrogenic origin in pelagic ocean regions has been well studied. The FMC may be significantly enriched in rare-earth elements but these may display well-expressed positive Ce-anomalies [3, 4, 10, 11, 24, 38]. Generally, the REE composition in pelagic oceanic concretions is a mirror-image of their composition in deep-water pelagic ocean zones [23, 45].

As the volume of data on REE in hydrothermal Fe-Mn formations on the ocean bottom increased, it became necessary to organize this data in order to establish the basic patterns for the makeup and accumulation of REE concentrates. In addition to the Fe- and Mn-hydroxides, the following forms of hydrothermal deposits are also enriched in these elements: recent metal-bearing sediments and their ancient analogs in the basal layers, at the base of the DSDP cores, crusts and concretions. Authigenic Fe-silicates (smectites and Fe-montmorillonites), in addition to Fe^{3+} , also contain Fe^{2+} that formed as the result of the interaction between Fe and SiO_2 ; both derived jointly from hydrothermal sources.

One of the main problems concerns the carriers and accumulators of REE in hydrothermal oxide and silicate deposits. In the axial zone of the East Pacific Rise (EPR), REE in the metal-bearing deposits are carried mainly by hydrothermal iron hydroxides and the REE concentration occurs during selective absorption from solutions of deep oceanic waters [8].

Our aim is to draw general conclusions on the basis of data in the literature on REE in hydrothermal Fe- and Mn-concentrates on the ocean bottom, in order to understand the genesis of these deposits and the general factors that control the composition of REE in them.

The literature, used in the paper, included data on REE, the composition of hydrothermal deposits and their locations (Table 1 and 2). In most cases, values of individual analyses of monotypic formations of similar composition, presented by individual workers, have been averaged in the Tables.

CLASSIFICATION OF HYDROTHERMAL Fe-Mn OCEANIC DEPOSITS

The forms and morphologies of hydrothermal concentrate products of Fe and Mn are very varied in the sediments. In addition to unconsolidated metal-bearing sediments that occupy extensive areas, especially on the bottom of the southwestern Pacific, and composed basically of x-ray amorphous Fe- and Mn-hydroxide precipitates and admixtures of varying amounts of biogenic CaCO_3 and lithogenic matter, sediment beds with high concentrations of iron occur near hydrothermal springs. These are Fe-silicates (smectite and nontronite), often of fine- or coarse-granular appearance. Significant amounts of Mn often occur in such deposits; sometimes as individual Mn-hydroxide crusts, on other occasions Mn-oxide and carbonate precipitates disseminated throughout smectitic clay beds. Mn-hydroxide crusts are also known on basalt outcrops, basal-metalliferous sediments at the base of cores of deep-water drill sites, Mn- or Fe-Mn crusts on the surface or in lower layers of sediments. Finally, concretionary forms also

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occur, developed from hydrothermal Fe and Mn-precipitates in surficial layers that in external appearance do not differ from oceanic FMC's that formed hydrogenetically.

The geochemical indices usually are applicable in establishing the hydrothermal character of bottom sediments. Indices with Al and Ti (Al/Al + Mn + Fe, Al/Mn + Fe, Mn + Fe/Ti, and others), for such substances as oxidized concretions and crusts in which the Mn and Fe occur in ore concretions, could not be utilized.

It may be assumed that the composition of the hydrothermal Fe-Mn substances on the ocean bottom are characterized by variable Fe/Mn ratios and low concentrations of Co, Ni, and Cu [13]. The last feature distinguishes them from pelagic (so-called "hydrogenic") concretions and crusts. Another indicator of the hydrothermal genesis of Fe and Mn may be the rare earth element composition in oxides and silicates. It has been noted in numerous publications, dealing with REE in hydrothermal-sedimentary oceanic deposits, that their REE composition is the same as that of deep pelagic ocean water bodies. Negative Ce anomalies are typical within the REE [1, 2, 7, 9, 12, 39], described either by the Ce/Ce*† value or, in the simplest form, by the value of the Ce/La ratio.

Data on the Mn, Fe, Co, Ni, and Cu content in the Fe-Mn precipitates are shown in Table 1 and in the genetic diagram of marine Fe-Mn deposits, first presented by Bonatti et al. [13] (Fig. 1a). One of the present authors already pointed out that the Bonatti diagram can not be utilized in drawing genetic conclusions. However, the diagram is useful in reflecting patterns in the composition of Fe-Mn precipitates on sea and ocean floors [5]. Figure 1 shows that there is a broad range of Mn and Fe concentration values in hydrothermal deposits, along with a very wide range of Mn/Fe ratio values (between <0.01 and 268, Table 1). Co, Ni, and Cu values also displayed significant variations.

Based on the Fe and Mn concentrations and of nonferrous ores, some of these substances do not differ from "hydrogenic" pelagic concretions in the oceans (Table 1, samples 4-6 and 10). These concretions and crusts occur in the Bauer Depression, crusts of the Guatemala Basin (sample 3) and in Fe-Mn crusts in the Galapagos spreading center of the Pacific. Concretions of similar composition were found in the Guatemala Basin (sample 3) and in hydrogenic Fe-Mn crusts at the TAG site of the Atlantic (sample 14). These crusts grew on typical hydrothermal, high-Mn crusts in this Mid-Atlantic Ridge area where they developed over basalts (sample 13). Other samples (7, 11, 12, 30, 37a) have similar ore matter composition as hydrothermal metal-bearing sediments (5, 46), although as shown earlier, plots of samples from diagenetic concretions from marginal pelagic ocean zones [5] also fall within this field.

It follows that the concentration values of Co, Ni, and Cu and their totals can not serve in identifying a hydrothermal origin of Fe and Mn accumulations in ocean sediments.

The lower diagram field, along the Fe-Mn side of the triangle (described in publication [13] as of "hydrothermal" genesis) includes a number of data points. The field includes hydrothermal oxidized crusts, primarily of Mn-composition (sample 8) and Fe-Mn crusts (sample 9) from the Galapagos Spreading Center and the TAG field (sample 13); x-ray amorphous Fe-products of the Dellwood Rise and the Galapagos Center (samples 19 and 21); Fe-Mn concretions and crusts from the FAMOUS location of the Atlantic (samples 15-17). This field in the diagram (Fig. 1a) includes the large group of Fe-smectites from hydrothermal zones of the Atlantic, and essentially, from the Pacific Oceans (Table 1). Within the composition range of the "hydrothermal" field, according to Bonatti, various diagenetic lacustrine and marine Fe-Mn concretions also occur. Their Fe/Mn ratios also show great variations and the Co, Ni, and Cu content is very low [5].

The composition of hydrothermal products may also be viewed in an Al-Si-Fe triangle diagram (Fig. 1b). All sediments with hydrothermal components are depleted in Al. For this reason, the Al-content is utilized in estimating the amount of lithogenic components in hydrothermal sediments. The composition of the lithogenic components of hydrothermal oceanic sediments is closest to that of deep water pelagic clays. The diagram (Fig. 1b) indicates the average composition of Pacific pelagic clays, in which the Fe/Al value is 0.6, the average Si/Al close to 3, with a range of 2.5-4.0. The Si/Al range in pelagic ocean deposits is indica-

† $Ce/Ce^* = \frac{\text{sample}}{Ce_{\text{shale}}} / \frac{1}{2} \left(\frac{La_{\text{sample}}}{La_{\text{shale}}} + \frac{Nd_{\text{sample}}}{Nd_{\text{shale}}} \right)$, where, Ce_{shale} , La_{shale} , and Nd_{shale} express the average concentration values of the elements in clayey shales of the continental platforms [38].

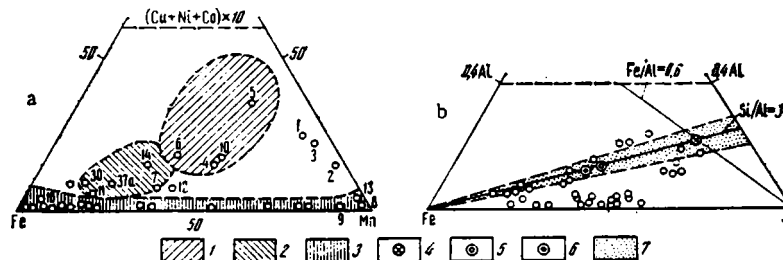


Fig. 1. Composition characteristics of hydrothermal formations (a - Mn-Fe-(Cu + Ni + Co)•10 - triangle; b - Fe-Al-Si - triangle). 1) Deep-water pelagic ferromanganese concretion and hydrogenic crust-field [13]; 2) field of hydrothermal, metal-bearing sediments and diagenetic concretions in marginal pelagic ocean zones [5, 46]; 3) field of hydrothermal Fe-Mn deposits [13] and shallow water diagenetic concretions of seas and lakes [5]; 4) average value of pelagic clays of the Pacific Ocean; 5) muds of the Bauer Depression; 6) deep-water pelagic ferromagnesian concretions; 7) Si/Al field = 2.5-4, typical of terrigenous clays and pelagic oceanic clays. Numbers at dots: number of samples, given in Tables 1 and 2.

ted by hatching in the triangle diagram. Also shown are the average compositions of ferromagnesian concretions of the Pacific and of the hydrothermal muds of the Bauer Depression. They are significantly enriched in Fe, in comparison with pelagic clays (based on the Fe/Al values), while their clay components (based on the Si/Al values) remain identical.

The dot distribution in the diagram (Table 1) shows that all deposits were depleted in Al and enriched in Fe. A significant portion (samples 1-14, 29, and 30) represents an Al-silicate clayey composition of pelagic clays, essentially of terrigenous origin, in which the Si/Al ratio is between 2.5-4.0; close to pelagic clay values. Consequently, the Fe-excess in these formations is represented primarily by oxides and hydroxides. Other sediments that represent minimum Al content in the data points of the diagram, with increased Si/Al values in Table 1, occur along the Fe-Si side of the triangle and reflect hydrothermal Fe-silicate composition. The Si/Fe weight ratio in nontronites is close to unity [30, 40]. According to the data of the diagram (Fig. 1b) the Si/Fe values are variable in hydrothermal deposits that are practically devoid of Al. This indicates the presence of either free SiO₂ or Fe-hydroxides. Finally, the Si/Fe values in Fe-silicates, as Si/Al values in Al-silicates do not remain constant. Even minor admixtures of Fe-montmorillonites, the presence of which is indicated in hydrothermal deposits [41], greatly increase the Si/Fe ratios.

X-ray amorphous Fe-precipitates (samples 19 and 21), along with hydroxides contain large amounts of Fe-silicates, while goethite with minor admixtures of smectite (sample 31 [44]), is composed almost completely of Fe-silicates.

Thus, all formations on the ocean floor that contain hydrothermal Fe, may be subdivided into two major groups: hydrothermal Fe- and Mn-hydroxides, with silicate admixtures of terrigenous clays; and silicates in which Fe is essentially composed of authigenic hydrothermal smectites or montmorillonites. Hydrothermal Fe-hydroxides and silicates may coexist in the sediments. The presence of hydrothermal Fe-silicates is well indicated by the Si/Al values in these substances.

REE COMPOSITION IN HYDROTHERMAL DEPOSITS

REE composition data in hydrothermal formations are shown in Table 2. In most instances (Table 1) they display the average of individual analysis results. The REE content varies within hydrothermal Fe- and Mn-substances within a very wide range. Table 2 indicates that the total-REE values had a range of 0.9-770 g/ton in the analyzed samples.

The REE concentrations in hydrothermal substances depend on the chemical and mineralogical composition of the deposits. Based on the REE behavior, all hydrothermal Fe and Mn concentrates may be subdivided in two clearly distinguishable subgroups; oxides and silicates. The problem of REE-carriers in hydrothermal deposits is an important one.

TABLE 1. Chemical Composition of Hydrothermal Mn and Fe Substances

Sample number	Location	Sample type	Sample number	Percentage composition of dry matter				Mn/Fe	Si/Al	Composition, n · 10 ⁻⁴ %			Reference
				Mn	Fe	Si	Al			Co	Ni	Cu	
1	Pacific Ocean, Guatemala	Fe-Mn concretion (upper portion)	25	35,9	3,78	4,30	2,05	9,5	1,9	216	8040	4370	[21]
2	Same	Same	27	43,8	1,11	2,08	1,01	39,5	2,1	82	5310	1720	
3	»	Same (bulk analysis)	23	38,8	2,92	3,84	1,72	13,2	2,2	195	7420	3710	
4	»	Fe-Mn crusts	3	21,7	17,4	4,93	1,17	1,2	4,2	1210	5440	650	[22,46]
5	Pacific Ocean, Bauer Depression	Fe-Mn concretions	5	27,0	9,0	5,58	1,36	3,0	4,1	887	12360	6610	
6	Same	Fe-Mn crusts	2	15,5	20,0	5,4	1,4	0,8	3,9	1120	4670	2390	
7	Pacific Ocean Ridge	Same	5	12,0	19,0	11,5	2,44	0,6	4,7	390	1560	390	[46]
8	Juan de Fuca	Mn-crusts	13	49,5	0,2	0,61	0,19	236	3,2	10	389	98	[18,34, 35,46]
9	Pacific Ocean, Galapagos Spreading Center	Mn-crusts, with admixture of Fe	5	42,0	3,3	8,31	1,77	12,7	4,7	25	385	159	[34]
10	Same	Fe-Mn crusts	3	21,1	14,7	5,17	1,33	1,4	3,9	553	6200	572	[18,35]
11	Pacific Ocean, EPR	Fe-Mn concretion and crust	2	7,9	29,4	5,3	1,5	0,3	3,5	317	880	1320	[46]
12	Pacific Ocean, Hess Deep	Fe-Mn crusts	1	16,7	21,8	—	0,31	0,8	—	508	1950	735	[15]
13	Atlantic, Ocean, TAG hydrothermal field	Mn-crusts, basal layer	5	42,9	0,16	0,73	0,18	268	4,0	30	880	445	[46]
14	Same	Hydrogenic Fe-Mn crusts (surface layer No. 13)	4	10,7	20,4	5,3	1,9	0,5	2,8	2590	1720	817	
15	Atlantic Ocean, FAMOUS-location	Mn-Fe concretion	1	26,8	11,4	7,8	0,9	2,4	8,7	91	570	275	[25]
16	Same	Fe-Mn crust	1	8,3	28,4	11,5	0,2	0,3	57,5	10	225	135	
17	»	Same	1	31,0	6,8	4,7	0,5	4,6	9,4	83	163	143	
18	»	Smectite	3	3,3	24,8	18,1	0,07	0,13	258	5,4	9,3	40	[25,46]
19	Pacific Ocean, Dellwood Rise	X-ray-amorphous Fe-matters	2	1,8	33,3	8,9	0,5	0,05	17,8	6,5	51	8,8	[17,46]

20	Pacific Ocean, hydrothermal field near the Galapagos spreading center	Nontronites	5	0,44	19,3	20,0	0,45	0,02	44	4,3	41	50	[18]
21	Same	X-ray-amorphous Fe-matters	2	7,9	27,5	13,3	0,32	0,3	42	3,2	63	48	
22	Southern flank of Galapagos spreading Center, DSDP, Leg 70	Fe-smectite, fine-grained	14	0,15	22,5	24,4	0,52	<0,01	47	2,5	10,2	28	[34]
23	Same	Fe-smectite, fine-grained	3	2,1	18,2	23,1	1,70	0,1	13,6	19,8	81	123	
24	»	Al-Fe smectite	2	0,14	11,7	25,9	4,9	0,01	5,3	9,2	63	140	[20,26]
25	»	Fe-smectites	6	0,08	20,9	24,6	0,15	0,004	164	4,7	15	46	
26	Same	Same, with Al-admixture	2	0,09	18,4	23,3	1,1	0,005	21	7,5	33	114	[26]
27	»	Same, Mn-oxide admixture	2	2,85	19,6	22,7	0,35	0,15	65	3	23	68	
28	»	Fe-smectites, with Al-admixture, in mixture with Mn oxides	4	5,94	9,9	21,8	3,54	0,6	6,2	24	179	172	[20,26]
29	»	Basal sediments	2	2,22	8,93	22,8	4,66	0,25	4,9	33	205	215	
30	Pacific Ocean, southern basin, buried hydrothermal deposits	Zeolitic red clays (top of core)	5	4,26	19,86	11,86	4,51	0,2	2,6	214	1014	1010	[20]
31	Same	Goethite with minor smectite admixture from zeolitic clays	1	0,67	18,8	19,6	1,07	0,04	18,3	50	225	160	
32	»	Nontronitic layer (from core)	8	4,18	21,0	22,29	0,13	0,2	171	<20	153	70	[46]
33	»	Nontronite	1	0,06	25,04	23,53	0,02	<0,01	1276	10	6	none	
34	»	Mn-layer (bottom of core)	7	17,83	14,65	14,78	0,55	1,2	27	64	690	833	[36]
35	»	Todorokite from Mn-layer	1	26,5	6,77	5,41	0,05	3,9	108	none	1390	1020	
36	»	Oxidized layers (bottom of core)	4	5,49	21,28	17,02	1,70	0,26	10	128	380	413	[36]
37a	Tyrrhenian Sea, southern area	Fe-Mn crusts	5	5,23	18,2	14,3	5,2	0,28	2,8	492	1217	411	
37b	Same	Same	5	1,93	28,1	9,3	0,97	0,07	9,6	191	101	157	

TABLE 2. Rare Earth Element Composition in Hydrothermal Fe- and Mn-Deposits, g/ton

Sample No.	La	Ce	Nd	Sm	Eu	Tb	Yb	Lu	Σ REE	Ce/La	La/Yb	Reference
1	16-56 36,4 (11)	10-68 42,6 (11)	14-48 32,2 (11)	3,0-9,8 6,9 (11)	0,76-2,43 1,94	0,60-1,61 1,14 (11)	2,9-7,4 5,7 (11)	0,47-1,14 0,85 (11)	47,7-194 127	0,63-1,45 1,13	6,4	[37]
2	8-16 11,5 (13)	8-16 11,2 (13)	8-13 10,3 (13)	1,4-2,7 2,2 (13)	0,40-0,68 0,51 (13)	0,19-0,51 0,37 (13)	1,5-2,8 2,0 (13)	0,24-0,46 0,32 (13)	33,0-51,1 38,5	0,57-1,50 1,01	5,8	
3	12-35 20,5 (6)	12-38 19,7 (6)	11-31 19,0 (6)	2,3-6,9 4,0 (6)	0,77-1,70 0,99 (6)	0,41-1,27 0,70 (6)	2,2-6,0 3,5 (6)	0,34-0,92 0,55 (6)	40,8-121 68,9	0,76-1,09 0,95	5,9	
4	131-136 134 (2)	196-210 203 (2)	109-114 112 (2)	23-25 24 (2)	6,10-6,22 6,16 (2)	3,55-3,68 3,62 (2)	18-19 18,5 (2)	2,64-2,89 2,77 (2)	503-503 503	1,44-1,60 1,52	7,2	
5	67,0-90,2 77,8 (5)	65,4-115 91,7 (5)	6,32-84,7 72,7 (4)	13,2-17,6 15,1 (5)	3,62-4,80 4,23 (5)	2,8 (1)	10,8-13,7 12,4 (5)	2,6 (1)	186-380 315	0,98-1,21 1,17	6,3	[22, 46]
6	121-246 184 (2)	123-182 153 (2)	98,2 (1)	20,0-43,6 31,8 (2)	5,44-10,4 7,9 (2)	7,4 (1)	15,6-22,9 19,3 (2)	4,3 (1)	450-516 483	0,74-1,02 0,88	9,5	
7	146-174 156 (5)	148-230 185 (5)	—	29,9-37,5 34,0 (5)	1,0-10,9 8,0 (5)	4,5-5,5 5,0 (5)	20,3-28,0 24,0 (5)	3,2-3,9 3,6 (5)	367-470 416	1,01-1,40 1,16	6,5	[46]
8	0,8-23,3 4,3 (13)	0,5-8,7 2,6 (13)	0,4-19,5 7,1 (3)	0,07-3,83 0,72 (11)	0,03-1,25 0,23 (13)	0,01-1,00 0,16 (13)	0,17-6,82 0,93 (13)	0,05-1,13 0,22 (13)	2,3-64 10,9	0,31-2,1 0,86	4,6	[17, 18, 34, 46]
9	13,4-13,6 13,5 (7)	12,5-14,6 13,1 (7)	—	2,11-2,45 2,21 (7)	0,49-0,64 0,60 (7)	0,52-0,59 0,57 (7)	1,99-2,06 2,01 (7)	0,29-0,38 0,32 (7)	31,7-33,9 32,3	0,92-1,09 0,97	6,7	[34]
10	92-219 162 (3)	113-281 200 (3)	73-173 126 (2)	15,5-37,3 26,6 (3)	4,3-9,4 7,5 (3)	2,7-6,8 5,0 (3)	14,0-27,9 23,2 (3)	2,4-5,4 4,0 (3)	317-765 512	1,18-1,28 1,23	7,0	[17, 18]

11	<u>156--246</u> 201 (2)	<u>76--182</u> 129 (2)	---	<u>23,8-43,6</u> 33,7 (2)	<u>7,5--10,4</u> 9,0 (2)	<u>5,2--7,4</u> 6,3 (2)	<u>21,3--22,9</u> 22,1 (2)	<u>3,5--4,3</u> 3,9 (2)	<u>293-516</u> 405	<u>0,49-0,74</u> 0,62	9,1	[46]
12	331 (1)	77	256	45	10,4	8,5	37	5,9	771	0,23	8,9	[15]
13a	<u>3,1-4,0</u> 3,55 (2)	<u>0,5-1,7</u> 1,1 (2)	---	<u>0,55-0,93</u> 0,74 (2)	<u>0,17-0,29</u> 0,23 (2)	<u>0,14-0,19</u> 0,17 (2)	<u>0,49-1,40</u> 0,95 (2)	<u>0,08-0,18</u> 0,13 (2)	<u>6,2-7,5</u> 6,9	<u>0,13-0,54</u> 0,31	3,7	}
13	<u>5,1-10,1</u> 7,6 (2)	<u>0,7-5,8</u> 3,3 (2)	---	<u>1,1-2,0</u> 1,6 (2)	<u>2,3-6,2</u> 4,3 (2)	<u>0,12-0,37</u> 0,25 (2)	<u>1,0-1,8</u> 1,4 (2)	<u>0,27-0,28</u> 0,28 (2)	<u>10,6-26,5</u> 18,6	<u>0,14-0,57</u> 0,43	5,4	
14	<u>235-295</u> 266 (3)	<u>960-970</u> 963 (3)	---	<u>50,0-62,5</u> 54,8 (3)	<u>1,3-12,8</u> 5,2 (3)	<u>0,8-6,2</u> 4,0 (3)	<u>24,6-29,0</u> 26,5 (3)	<u>1,4-3,3</u> 2,6 (3)	<u>1307-1340</u> 1322	<u>3,25-4,09</u> 3,66	10,0	
15	5,7 (1)	6,5	5,4	1,07	0,26	0,20	0,94	0,18	20,3 (1)	1,14	6,1	}
16	4,0 (1)	1,87	2,4	0,40	0,105	0,09	1,10	0,25	10,2 (1)	0,47	3,6	
17	6,3 (1)	6,2	---	1,2	0,28	0,25	0,69	0,1	15,2 (1)	0,98	9,1	[46]
18	<u>0,4--3,7</u> 1,7 (3)	<u>0,54-3,3</u> 1,7	<u>0,3-3,1</u> 1,5	<u>0,06-0,63</u> 0,30	<u>0,02-0,19</u> 0,09	<u>0,015-0,16</u> 0,09	<u>0,4-1,7</u> 1,07	<u>0,08-0,34</u> 0,21	<u>1,8-13,1</u> 6,7 (3)	<u>0,89-1,35</u> 1,2	1,6	[14, 46]
19a	0,66 (1)	2,2	1,4	0,58	0,084	0,11	0,36	0,091	5,5 (1)	3,3	1,8	[40]
19	1,3 (1)	1,9	---	0,27	0,09	0,06	0,46	0,11	4,2 (1)	1,46	2,8	[46]
20	<u>2,2-5,3</u> 4,0 (5)	<u>2,2-4,8</u> 3,3	---	<u>0,49-1,2</u> 0,76	<u>0,15-0,25</u> 0,19	<u>0,04-0,20</u> 0,09	<u>0,30-1,2</u> 0,78	<u>0,03-0,22</u> 0,13	<u>5,5-13,2</u> 9,3 (5)	<u>0,42-1,05</u> 0,85	5,1	}
21	<u>6,6-6,8</u> 6,7 (2)	4,2 (1)	---	<u>0,61-0,96</u> 0,79	<u>0,21-0,32</u> 0,27	<u>0,13-0,16</u> 0,15	0,99 (1)	<u>0,09-0,15</u> 0,12	13,2 (2)	0,64	6,8	
22	2,5 (14)	3,9	---	0,95	0,17	0,14	0,60	0,10	8,4 (14)	1,56	4,2	}
23	37,8 (3)	25,0	---	6,5	1,7	---	3,5	0,50	75 (3)	0,67	10,8	
24	15,5	20,7	---	3,5	0,81	0,60	1,7	0,30	43 (2)	1,34	9,1	
25	<u>0,19-3,73</u> 0,96 (6)	<u>0,34-4,76</u> 1,23	<u>0,46-3,57</u> 1,0	<u>0,024-0,82</u> 0,22	<u>0,019-0,185</u> 0,056	<u>0,042-0,17</u> 0,070	<u>0,092-0,65</u> 0,26	<u>0,007-0,123</u> 0,043	<u>0,9-14</u> 3,8 (6)	<u>1,00-1,8</u> 1,38	3,7	[20, 26]

TABLE 2 (continued)

Sample No.	La	Ce	Nd	Sm	Eu	Tb	Yb	Lu	Σ REE	Ce/La	La/Yb	Reference
26	2,49 (2)	3,57	3,06	0,75	0,19	0,16	0,51	0,087	10,8 (2)	1,43	4,9	} [26]
27	1,26 (2)	1,73	1,59	0,33	0,093	0,085	0,32	0,064	5,5 (2)	1,37	3,9	
28	$\frac{3,3-20}{9,6 (4)}$	$\frac{6,0-20}{11,0}$	$\frac{3,0-20}{10,9}$	$\frac{0,6-3,7}{2,07}$	$\frac{0,16-1,1}{0,57}$	$\frac{0,16-0,63}{0,38}$	$\frac{0,61-3,9}{1,84}$	$\frac{0,12-0,52}{0,28}$	36,6 (4)	$\frac{1,0-1,8}{1,15}$	5,2	[20, 26]
29	31,5 (2)	77,5	64	7,8	2,3	2,05	11,75	2,25	199,2	2,45	2,7	[20]
29a	$\frac{3,12-3,4}{3,22 (3)}$	$\frac{9,72-12,2}{11,24}$	$\frac{11,6-12,75}{12,12}$	$\frac{3,98-4,30}{4,17}$	$\frac{1,52-1,75}{1,62}$	$\frac{1,17-1,32}{1,23}$	$\frac{4,67-5,36}{4,95}$	$\frac{0,85-0,98}{0,90}$	$\frac{36-42}{39,4 (3)}$	$\frac{3,11-8,87}{3,5}$	0,65	[26]
30	214 (5)	204	242	45,8	12,6	10,2	31,3	5,3	765 (5)	0,95	6,8	} [44]
31	9,4 (1)	20,4	9,2	2,25	0,6	0,5	1,53	0,26	44,1 (1)	2,17	6,1	
32	1,3 (8)	0,93	1,0	0,22	0,05	0,05	0,31	0,06	3,8 (8)	0,71	4,2	
33	0,5 (1)	0,54	0,4	0,11	0,03	0,03	0,14	<0,02	1,8 (1)	1,08	3,6	
34	4,0 (7)	4,8	3,5	0,58	0,13	0,10	0,55	0,09	13,8 (7)	1,20	7,3	
35	8,4 (1)	5,9	5,0	1,15	0,30	0,27	1,0	0,17	22,2 (1)	0,70	8,4	
36	12,5 (4)	43,0	13,0	2,85	0,80	0,55	1,6	0,27	74,6 (4)	3,44	7,8	
37a	$\frac{20,5-84}{58,5 (5)}$	$\frac{42-160}{112}$	$\frac{18,1-74}{49,2}$	$\frac{3,02-15,1}{10,0}$	$\frac{0,68-3,68}{2,43}$	$\frac{0,41-2,3}{1,48}$	$\frac{1,38-7,7}{4,93}$	$\frac{0,25-1,24}{0,81}$	$\frac{86-358}{240 (5)}$	$\frac{1,67-2,34}{1,92}$	11,9	} [36]
37b	$\frac{3,9-29,1}{13,6 (5)}$	$\frac{9,0-56}{26,8}$	$\frac{5,3-23,1}{11,6}$	$\frac{0,92-3,6}{1,92}$	$\frac{0,25-0,67}{0,42}$	$\frac{0,18-0,42}{0,30}$	$\frac{0,90-2,27}{1,67}$	$\frac{0,14-0,47}{0,33}$	$\frac{22-114}{57 (5)}$	$\frac{1,59-2,50}{2,0}$	8,1	

Notes. 1) In addition, in samples 5 and 6, respectively, the following values were found: Gd: 18.6 and 24.9; Dy: 18.6 and 25.2; Er: 12.6 and 16.4; 2) Sample 29a—basalts in drill cores of Leg 54; 3) in numerator: range of values; in denominator: average values; in brackets: number of analyses.

Data in Table 2 indicate that in deposits where the basic Fe and Mn species are hydroxides (Table 2, samples 1-13, 29, 30, 37a) the total concentration of REE increases almost proportionally with the Fe concentration increase. The reverse relationship between the REE content and Mn/Fe ratio is equally well-defined. Based on 80 samples, the coefficient of paired correlation for REE-Fe, using all the selected positions in Table 2, was established as 0.91- ($r_{crit} = 0.34$). The REE-Fe function in Fig. 2 ($r = 0.92$ at $n = 17$, $r_{crit} = 0.75$) was universal, as changes in the Mn/Fe values in the studied samples ranged from 0.2 to 270, including all conceivable Fe/Mn ratios in natural oxides of these elements.

This relationship between REE and Fe in hydrothermal hydroxides has been established for the first time, although, in general, it is trivial. Fe-hydroxides had been accepted as the prime carriers of REE in deep water oceanic ferromanganese concretions [2, 23, 24, 38]. The clearly proportional relationship between REE (La and Ce) and Fe has been shown in these concretions by the DOMES program in one of the area polygons [16]. In addition, we have already shown [7, 8] a REE-concentration mechanism from deep ocean waters, involving hydrothermal Fe-hydroxides and metal-bearing sediments of VTP.

If the Fe-hydroxides are the main carriers (concentrators) of REE in oxidized hydrothermal substances and a practically proportional relationship exists between REE and Fe (Fig. 2), then the specific REE accumulation in Fe-hydroxides should be sufficiently constant. Calculation of data found in Tables 1 and 2 indicated that the specific concentration (REE/Fe, in mg/g) in individual substances ranged between 1.0-3.8, with an average value of 2.7 mg REE for 1 g Fe. A higher specific REE concentration in Fe (5.5 and ~8.0 mg/g occurred only in two samples of high-Mn crusts (40% Mn), with low Fe-content (Tables 1, 2; samples 8 and 13). The total REE values were also minimal in them (average: not greater than 20 g/ton). In this case it is possible that at generally low REE levels, other secondary carriers start to play an increased role as carriers (Mn-dioxide?) in these crusts, that do not have a high absorptional capacity with respect to lanthanides. Only after recalculation, does an increased specific iron concentration appear to have taken place.

As shown [8], the value of specific REE concentration in Fe-hydroxides, and consequently, the REE concentrations in hydrothermal oxides, was determined by the time when contact occurred between Fe-hydroxides particles and deep marine waters during transport from the formation location (hydrothermal magma chamber) to the burial location on the ocean floor. The above presented values of specific REE concentration in Fe-hydroxides in the studied substances indicated that they developed in the immediate vicinity of hydrothermal spring areas. Only in sediments, located along the ridge axes or their immediate vicinity do such, relatively low values of specific REE accumulation occur in the Fe-hydroxides. All samples conditionally satisfy this condition, with the exception of Fe-Mn concretions and crusts of the Guatemala Basin and the Bauer Depression.

Certain hydrothermal oxide samples contain significant amounts of Al (Table 1). This shows that lithogenic matter is included that carries a certain amount of REE in the oxides. This substance consists of clayey matter, in certain samples products of basalt weathering (Tables 1 and 2; sample 29). The approximate amount of lithogenic components in the total amount of REE indicates that in most hydrothermal oxides the lithogenic carrier contains not more than 10% REE, while in individual samples the lithogenic components may represent 30-40% of the total amount of REE (samples 1-3, 9, 13, 29, 37a). This fact evidently is the main reason for the data scatter, shown in Fig. 2.

An entirely different picture emerges through the study of REE accumulation in sediments in which the basic form of Fe is in silicates of hydrothermal origin. Table 1 shows that their Si/Al ratios are higher than 5. In addition to smectites and nontronites this sample group also contains Fe-Mn concretions and crusts in the FAMOUS area (samples 15-17), Mn-layers and todorokite from the lower part of core 9KL in the Southern Basin of the Pacific (samples 34 and 35), x-ray amorphous Fe-substances (samples 19 and 21) and goethite (sample 31), half of the Fe-Mn hydrothermal crust samples from the Tyrrhenian Sea (sample 37b; Table 1). In the recalculated samples the Si/Al values ranged from 9.4 to 57.5, indicating that at least a significant part of their Fe content is in the form of silicates.

In these deposits low REE values typically range between 0.9-75 g/ton (Table 2). Most samples had an REE content of <20 g/ton. Only in a few samples (samples 23, 24, 28, 31 and 37b) were the REE values higher. Correlation between the REE and Fe content in silicate substances does not exist (Fig. 3a). A conditionally calculated specific REE-content in Fe in

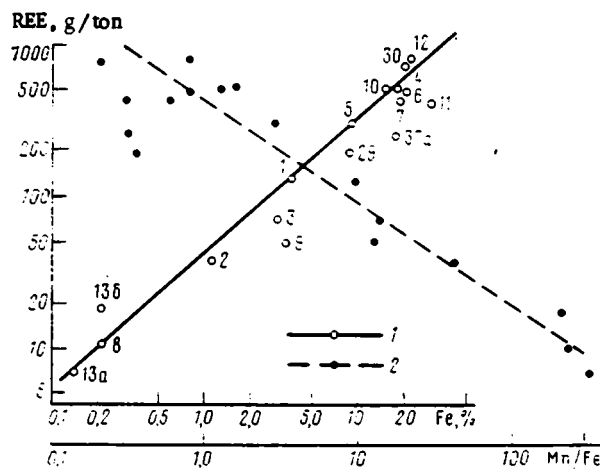


Fig. 2. Relationship between the REE content in hydrothermal oxide formations and the Fe content (1) and the Mn/Fe ratios (2). Numbers at dots: sample numbers, given in Tables 1 and 2.

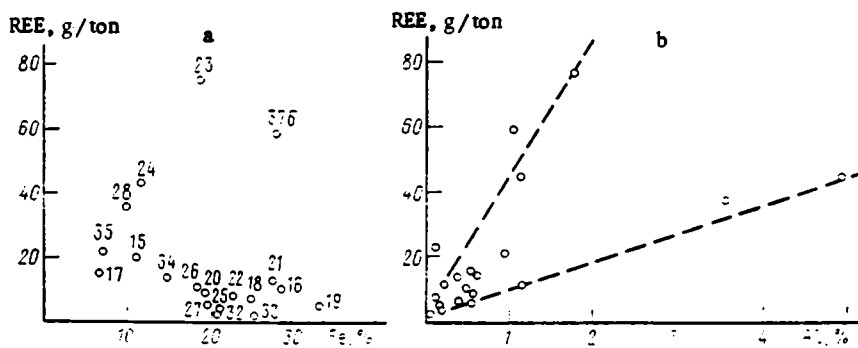


Fig. 3. Relationship between REE concentration in hydrothermal silicate substances and the Fe (a) and Al (b) content. Number at dots: sample number, as shown in Tables 1 and 2.

hydrothermal silicates ranges between <0.01 and ~ 0.4 mg/g. It is incomparably lower than in Fe of hydrothermal oxides.

Most samples with high (>20 g/ton) REE-content have high ($>1\%$) Al-content. Correlation of the REE and Al content in all selected hydrothermal Fe-silicates (Tables 1 and 2) have shown a statistically very significant positive correlation. The coefficient of paired REE-Al correlation of 20 samples was 0.81 ($r_{crit} = 0.66$; Fig. 3b). In order to exclude random error in averaging, the coefficient of paired correlation was also calculated for 40 individual analyses of Al and REE, resulting in an r -value of 0.78 . Finally, individual calculations were made of the coefficient of paired correlation of samples with Al-content of $<1\%$, with 30 analyses, $r = 0.72$. As with the absolute REE content (Fig. 3b), the specific concentration ($\Sigma \text{ REE/Fe}$, Mg/liter) in hydrothermal silicates was directly related to the Al-content ($r = 0.81$, with $n = 21$). It may thus be concluded that in hydrothermal silicates Fe displays an empirical relationship between the REE and Al content.

The established relationships indicate that hydrothermal Fe-silicates can not accumulate REE's and the REE content in these substances is not connected with Fe-accumulation. The slight REE increase above a low REE-background level in certain samples may be explained by Al-silicate admixtures, the main carrier of REE in such matters. In certain samples with hydrothermal silicates, a mixture of free Fe-hydroxides may occur that also increases the REE concentration values (presumably samples 24 and 31). If one disregards the presence of Al in hydrothermal solutions, then lithogenic (terrigenous) clayey matter and material from the destruction of basalts may be carriers of REE. If either of these occur in mixtures of hydrothermal silicates with iron, they increase the REE content in the iron. At the same time, the presence of terrigenous clayey and basalt matter may change the REE content, in comparison

with lanthanide content in deep ocean waters, the main source of REE for the hydrothermal formations of the ocean.

COMPOSITION AND GENESIS OF REE OF HYDROTHERMAL SUBSTANCES

The composition of REE in hydrothermal hydroxides and silicates is shown in Table 2. The REE composition in Fig. 4, given after standardization for mean REE values, is shown in the clayey shales of continental platforms [38]. In most samples the REE content is typical of dissolved REE content in oceanic waters, with a Ce-deficit and increased role of the heavy lanthanide elements. In addition, the REE-values in individual hydrothermal Fe-Mn substances are close to those of terrigenous and basaltic matters. Only in one sample has a positive Eu-anomaly clearly been identified, derived from REE's of high-temperature hydrothermal solutions [32, 33].

The enrichment of hydrothermal Fe and Mn hydroxide concentrates with rare element concentrations, traditionally and with good reason has been attributed to REE-extraction from oceanic waters. With few exceptions, the known or assumed hydrothermal springs on the ocean floor occur at depths greater than 2000-2500 m. Therefore, the REE-extraction and the enrichment of hydrothermal Fe-hydroxides in REE is only possible from deep oceanic waters.

The basic sources of dissolved REE in ocean waters are fluvial solutions and suspendates. The REE composition in fluvial discharge is similar to the average REE content of clayey shales [38], in which the Ce/La ratio is 2; the ratio of La and heavy lanthanides, expressed as La/Yb, 11.6. A general pattern in the composition change of dissolved REE in ocean waters reflect the appearance and increase of a Ce-deficit (negative Ce-anomaly) with increasing distances from the nearshore zone in the pelagic region, and with increasing depths. The ratio of heavy REE [1, 6] also increases, due to the more intensive introduction of Ce into suspension and sediments, as well as due to the oxidation of Ce^{3+} and Ce^{4+} and increased stability of heavy REE and Y in the solution, owing to the greater stability of their complex compounds. As the result, the deep waters of pelagic regions of the open ocean will have lower Ce/La and La/Yb values, in contrast with sedimentary rocks of the continents.

Fig. 5a shows dissolved REE compositions in deep (>2000 m) ocean waters within the Ce/La and La/Yb coordinates, based on data in [27, 29, 31]. In deep waters the REE field is characterized by values of Ce/La < 1 (to 0.06) and La/Yb values of 3-7. The REE composition in hydrothermal substances, studied by the present authors, is indicated within the same coordinates (Fig. 5b). This shows the REE composition field in deep waters, of basalts in the spreading zone [42, 43], and the average composition of clayey rocks of continental rocks [38]. A large portion of the samples with hydrothermal iron hydroxide and silicate concentrates carries a REE content that is either identical with the composition of deep waters or very similar to it (Fig. 5b). The inadequate correlation between the composition of the absorbed complex and the composition of deep ocean water still requires explanation. As we have shown, absorption of REE from marine water solutions is a selective process [8]. The absorbed REE do not completely replicate the composition of the solution but are enriched in Ce and depleted in heavy lanthanides. The enrichment is the more pronounced process. Thus, data in Fig. 5 confirm that deep ocean water is the main REE source in the overwhelming majority of hydrothermal formations.

In addition, hydrothermal crusts, taken in the southern Tyrrhenian Sea by dredge at 500-900 m on island slopes contained practically pure-terrigenous (shaley) REE composition (sample 37a, 37b). This is not remarkable as the REE, dissolved and suspended in water of near-shore ocean zones and Mediterranean seas, have practically the same composition as the REE do in shales [1, 6]. The composition differences are minor in these crusts: in sample 37b the Fe-silicates have significant concentrations and minor amounts of the total REE, in comparison with purely oxide-bearing varieties (sample 37a), enriched in heavy lanthanides (La/Yb = 8.1).

It is more difficult to explain the Ce/La rare earth ratio in sample 31 that has been identified [44] as goethite, with minor admixture of smectite. Chemical data (Table 1) indicates practically pure smectite. The hydrothermal origin of these substances is without any doubt. The REE composition apparently may have resulted from a given mixture of deep ocean waters and basalt matter.

Certain samples contain REE that resulted from the mixture of basalts and varying amounts of REE from deep ocean waters (samples 19, 22, 29). Samples 19a and 19b represent two analyses of hydrothermal, x-ray amorphous substances from the Dellwood Rise [17, 46], but the chemical analyses show them (Table 1) as containing significant amounts of Fe-silicates. The REE

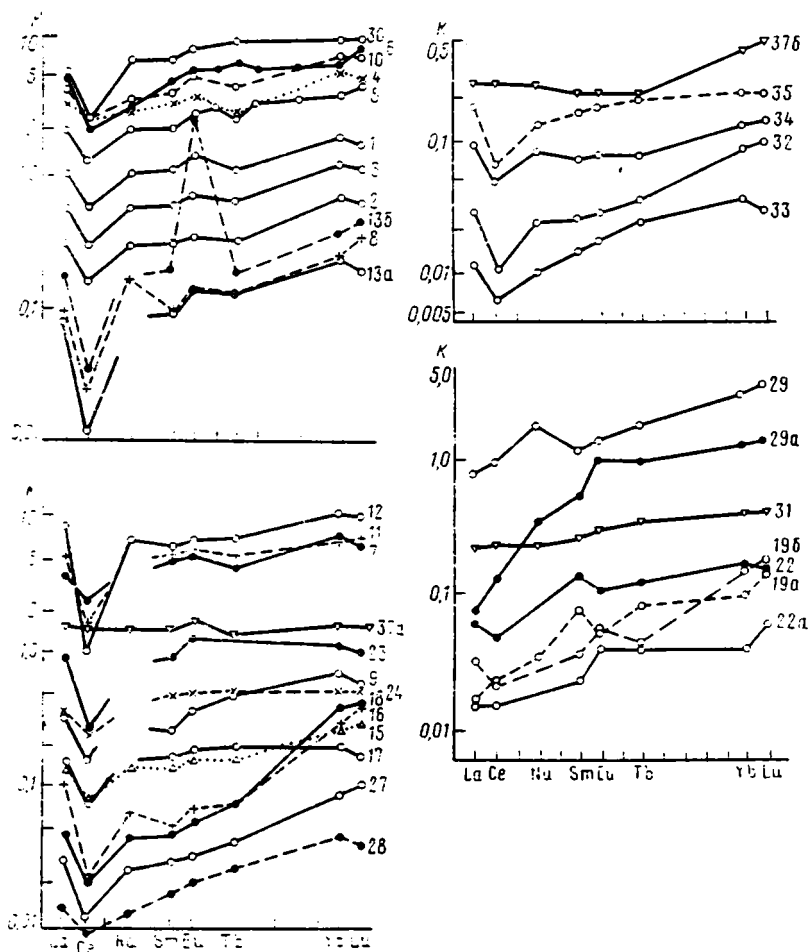


Fig. 4. REE content in hydrothermal Fe and Mn concentrates (standardized for REE in shale, $K_{\text{sample}}/S_{\text{shale}}$). Numbers by the curves: sample number of Table 2 (22a — average from two samples of smectite, from publication [34]).

content of sample 19a is very close to that of basalt (Fig. 4, Fig. 5b), while sample 19b contains significant admixture from deep ocean water. The REE in samples 22 and 22a (Fig. 4) contain lanthanides from two sources; from deep ocean water and basalt matter. These samples are represented by granular Fe-smectites from the southern flank of the Galapagos Spreading Center [34]. The visible presence of basalt matter in a mixture with ocean waters is apparent in sample 29 that contains metal-bearing sediments in deep-water drillcores [20]. The underlying, unaltered basalt is represented by sample 29a; Fig. 4.

The REE content in the basal layer of high-Mn hydrothermal crusts (Tables 1, 2, sample 13) is of interest. Four REE-analyses of these crusts [46] indicate that at low total-REE concentration the rare earth element makeup results entirely from sorption from deep ocean waters (Fig. 5). However, in two out of four analyses an anomalous high Eu-composition (sample 13b, Table 2, Fig. 4) occurred. In this very sample the outer lanthanides also displayed a higher concentration. The author [44] did not pay attention to this REE anomaly in the studied crusts. The sole source of REE, known presently with the potential for the high Eu-anomaly may be the hydrothermal solutions themselves. A positive Eu-anomaly and significant deficit in heavy lanthanides occur in the REE of high-temperature hydrothermal solutions at 13° and 21° N. The East Pacific Rise [32, 33] contains a clearly expressed Eu-anomaly and marked deficit in heavy lanthanides. The magnitude of the anomaly, expressed in Eu/Sm in weakly diluted solutions, ranges between 1.32-3.18 (average: 2.2). For comparison, in deep ocean waters at 13° N the Eu/Sm is 0.27; in sedimentary clays, 0.21. In exhalational-sedimentary substances the high Eu-content in the REE occurs only in the ore-bearing sediments of the Atlantis II Basin, Red Sea where the average Eu/Sm value is 0.44 and the range within individual horizons of three studied cores: 0.26-0.75 [19]. In sample 13b the Eu/Sm ratio is

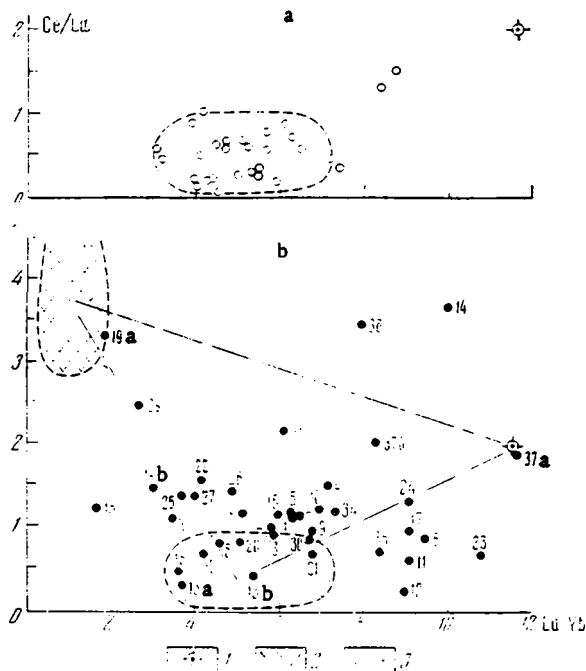


Fig. 5. REE content, with coordinates of Ce/La and La/Yb-ratios (a — water depth of oceans; b — hydrothermal concentrates of Fe and Mn): 1) average shale content; 2) basalt composition-field; 3) field of deep ocean water. Numbers at dots: sample number, given in Table 2,

2.7 that corresponds to a practically pure hydrothermal composition. In addition, with the exception of the Eu-maximum, the REE contain no other indications of hydrothermal origins and are identical in composition with those of deep ocean waters. Thus one can not attribute the REE composition of sample 136 to a mixture of lanthanides from a hydrothermal solution and deep ocean waters of two sources. Consequently, the Eu-anomaly either resulted from analytical error, or we are wrong as to the REE composition of the hydrothermal solutions, as obtained at two locations of the East Pacific Rise, along the entire rift zone and transform fault system of the ocean floor.

The basal hydrothermal crusts, essentially of Mn-composition (sample 13) are overlain by hydrogenic Fe-Mn crusts (sample 14) that contain Cu, Ni, Co (Table 1) and REE (Table 2, Fig. 5b) in proportions that are typical of sedimentary hydrogenic substances, similar to deep water, pelagic Fe-Mn concretions in the oceans.

In conclusion, briefly the results of the study of REE distribution in hydrothermal Fe- and Mn-hydroxides and silicates:

In hydroxides, the REE total ranges between c.20 and 770 g/ton and is characterized by the presence of Fe in mixed Fe-Mn-hydroxides. The REE-concentration and Fe-content are linked, as the rule; the Mn/Fe ratios show a wide range (<0.2-270). This confirms the conclusion that in mixed Fe-Mn substances, Fe-hydroxides are the main carriers and concentrators of REE.

Hydrothermal Fe-silicates (smectites and nontronites) are characterized by REE concentrations (0.9-75 g/ton) that are one order of magnitude lower. The REE content in hydrothermal silicates does not depend on the Fe content but is determined by the amount of admixed Al silicates, shown by the excellent correlation between REE and Al. The nature of Al-silicates in hydrothermal formations requires special studies. The presence of terrigenous clay admixture and products of basalt decomposition may be helpful in this respect. Authigenic hydrothermal Al-silicates may also have formed.

The review of data on the REE composition in hydrothermal formations indicates that in most instances REE accumulation occurs through interaction between hydrothermal substances and deep ocean water. This is satisfactorily shown by the Ce/La and La/Yb ratios in the REE of hydrothermally produced substances.

Oceanic deep water is practically the sole REE source for hydrothermal oxides in rift zones. Low Ce/La and La/Yb values in the REE are typical here. Such a composition occurs only in open oceanic hydrothermal deposits. In mediterranean seas with hydrothermal Fe-Mn crusts (e.g., Tyrrhenian Sea) the REE composition is practically identical with that of continental sedimentary rocks that, in turn, reflect the dissolved REE composition in such basins. One may assume that an REE composition that is close to the terrigenous content may be expected in hydrothermal substances in nearshore areas of oceanic sedimentation. Thus the ratio of the total REE in hydrothermal hydroxide deposits in the open ocean approximates that of deep waters and is a dependable indicator of their genesis. A significant admixture of lithogenic components within hydrothermal Fe- and Mn-hydroxides do not mask those aspects of the REE composition that point to deep oceanic water sources.

Hydrothermal Fe-silicate deposits usually form in the immediate vicinity of hydrothermal springs of the seafloor, while the dominant REE fraction from deep water sources may carry in their composition significant traces of basaltic decomposition products, with characteristic REE ratios.

The question of possible REE-fixation in hydrothermal hydroxide and silicate-bearing sediments by hydrothermal fluids of typical composition (Eu-maximum, heavy REE deficit, in comparison with chondrite or shale) is an unresolved one. It may be expected that this question would be resolved by the use of REE data on massive hydrothermal sulfides of the East Pacific Rise. This also applies to the problem on the REE genesis in sediments of mixed composition in the Atlantis II Basin (Red Sea). These sediments are very difficult to interpret.

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CLAY MINERALS OF LOWER AND MIDDLE JURASSIC SEDIMENTS OF STRUCTURAL AND FACIES ZONES OF THE CENTRAL CAUCASUS

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With special reference to Lower and Middle Jurassic sediments of the Central Caucasus the history of formation of clay mineral associations in various structural-facies zones of the northern margin of the Greater Caucasus geosyncline is traced from sedimentogenesis and diagenesis to epigenetic alteration of rocks at high temperatures. Sources of materials and sedimentation settings are examined as factors in creating the mineral composition of clay rocks during sedimentogenesis and diagenesis. The initial composition of sediments is demonstrated to have a strong influence on the formation of mineral associations at high temperatures.

The purpose of this study is to describe the features of the mineral composition of clay sediments which accumulated in various structural and facies zones of the early and medial Jurassic basin in the Central Caucasus and to trace the direction of clay material alteration in rocks affected by high temperatures.

Lower and Middle Jurassic rocks, widespread in the southeastern Labino-Malka zone, were studied; this territory is the former southern extremity of the Epihercynian Scythian platform within the Tyrnyauz-Pshekish suture zone and in the Kyrtyk depression (Fig. 1).

During the early and medial Jurassic the Scythian plate in the area under study was the scene of accumulation and erosion of largely continental sediments (Pliensbachian-early Toarcian); later it became the shelf of an expanding water basin.

The Kyrtyk depression is the eastern part of the Arkhyz-Guzeripl structural-facies zone, which during the early and medial Jurassic was the northern side of the geosynclinal trough of the Greater Caucasus [16]. The trough was separated from the Scythian platform by the Tyrnyauz-Pshekish suture zone; narrow trenches bounded by faults developed within that zone and at times cordillera-type rises were formed along these faults [15].

Because of the territorial proximity of the sections studied, sediments accumulated in different structural and facies zones subsided in the postsedimentary period to approximately the same depth under the overlying strata. They experienced largely similar catagenetic alterations. For example, measurements of the reflectivity of vitrinite from the coal seams at the base of Labino-Malka sections and the Kyrtyk depression showed that the specimens belong to the gas coal grade (G grade) on the coal metamorphism scale. It corresponds approximately to middle catagenesis. Clayey schists from the Tyrnyauz-Pshekish suture zone (Mukulan suite) were subjected to considerable heating during the Neogene, probably mainly because of intrusions that were formed there. As a result, Jurassic rocks were altered much more than were neighboring sections to the north and the south.

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Within the Labino-Malka zone the Lower and Middle Jurassic strata have been studied along the Tyzyl River (the left tributary of the Baksan River).*

At the base of the section is the Khumarin suite of the Lower Pliensbachian age (Figs. 2 and 3), consisting of argillite, conglomerate-gristone, and quartz sandstone members. The argillite member (up to 15 m thick) fills a depression in the pre-Jurassic relief and wedges out along the course. The argillite is dark brown with unclear layers. Imprints of leaves and stems of subaerial plants are often found on bedding planes. The argillites contain several coal interlayers and lenses (up to 0.1 m) and several layers of siderite nodules. The sediments of this member are classified with the group of facies of swamping lakes and peat bogs.

Coarse-clastic rocks in the suite are interpreted as deluvial-proluvial detrital fans and tails; the quartz sandstones with multistory oblique stratification are interpreted as the riverbed facies of alluvial sediments.

Continental sediments of the Khumarin suite are overlain with an erosion by the strata of the Dzhigiat suite, which accumulated in a marine basin. The suite consists of three parts: Lower Gizhgut (Middle Toarcian), Upper Gizhgut (bottom of the Upper Toarcian), and Baksan (the top of the Upper Toarcian-Aalenian) layers.

The Lower Gizhgut layers (80-90 m) consist mainly of interstratified argillite, siltstone, and sandstone beds. The argillites display no distinct stratification and range in color from gray to dark-gray with a brownish tinge. Fine coaly detritus is seen on bedding planes in the siltstones. Numerous siderite nodules are found in some intervals in argillites and siltstones. There are features indicating that the sediments accumulated in a transitional zone from shoals to moderately deep-sea conditions.

The Upper Gizhgut layers (50-60 m) consist of light-gray small-grained sandstone with several beds of gray siltstone; a significant presence of clay material appears in the roof of the sand horizon. The sediments accumulated in a sea shoal in conditions of active hydrodynamics.

Baksan layers (60-65 m) are argillite with interlayers of nodules, nodular conglomerate, and oolitic pyrite beds. The argillites are dark gray, sometimes greenish; the stratification is absent or blurred; siltstone varieties are predominant. Bedding surfaces exhibit traces of crawling organisms. Beds with ferruginous oolites, from a few decimeters to 2 m thick, are typical for the Aalenian stratum. Most oolites consist of goethite or hydrogoethite, although some oolites consist of ferruginous chlorite. Oolites are found also in argillite — mainly in interstratifications with oolite-containing beds, but there they are scarce and flattened, sometimes their fragments being found. An analysis of the characteristics of Baksan layers shows that they were accumulated in shallow zones with relatively active hydrodynamics.

The Dzhor suite (Bajocian) occurs with an erosion on the underlying bed [2]. The sediments consist mainly of gray and dark gray argillites, which are unevenly silted; siltstones are of secondary importance. A member (40 m) with interstratified sandstone layers (0.25-1.7 m) and gray silty clays has been described at the base of the suite. Nodular interlayers occur with interruptions of a few meters. The suite in the portion of the profile studied is approximately 270-300 m. These rocks accumulated in the open sea far from the shore, initially in shallow areas and later in deeper parts of the shelf.

At the center of the Kyrtyk depression (see Fig. 2), where the study was conducted, a thick (about 1200 m) Pliensbachian-Toarcian bed has been described [16]. The Lower Pliensbachian part of the section consists mainly of coarse sediments. In the basal horizon (20-25 m) lens-shaped beds of conglomerates, gritstone, sandstone, and micaceous siltstone are seen in an interstratification; they are not consistent along the course. Sandstones and siltstones contain lens-shaped coal seams (a few centimeters thick). Further up the section is an alternation of members and beds of sandstones, which are sometimes obliquely stratified and include gritstone and coal lenses; there are also members of clayey siltstone and argillite. Imprints of land plants are mostly seen in the bedding planes in the bottom portion of the bed. The Lower Pliensbachian is 250-280 m thick; the Upper Pliensbachian (up to 600 m) consists of dark-gray argillites with a brownish shade; these sediments are unevenly silty and contain lens-shaped sandstone interlayers in the middle portion. The Toarcian part of the section consists mainly of argillites up to 350 m thick. The Lower Jurassic in the Kyrtyk de-

*For a detailed description of the section, see [6].

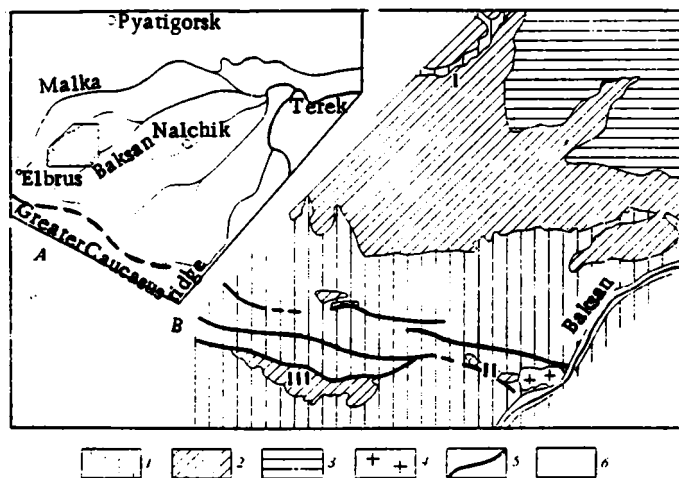


Fig. 1. Map of the area of study (A); geological structure of the left bank of the Baksan River in the area of study (B): 1) Paleozoic; 2) Lower and Middle Jurassic; 3) Upper Jurassic; 4) granitoid of El'dzhurta massif; 5) disruptive faults of Tyrnyauz-Pshekish suture zone; 6) Quaternary sediments of the Baksan River Valley. Roman numerals identify the sections: I) right bank of the Tyzyl River, Labino-Malka zone; II) Mukulan suite, Tyrnyauz-Pshekish zone; III) Kyrtyk depression.

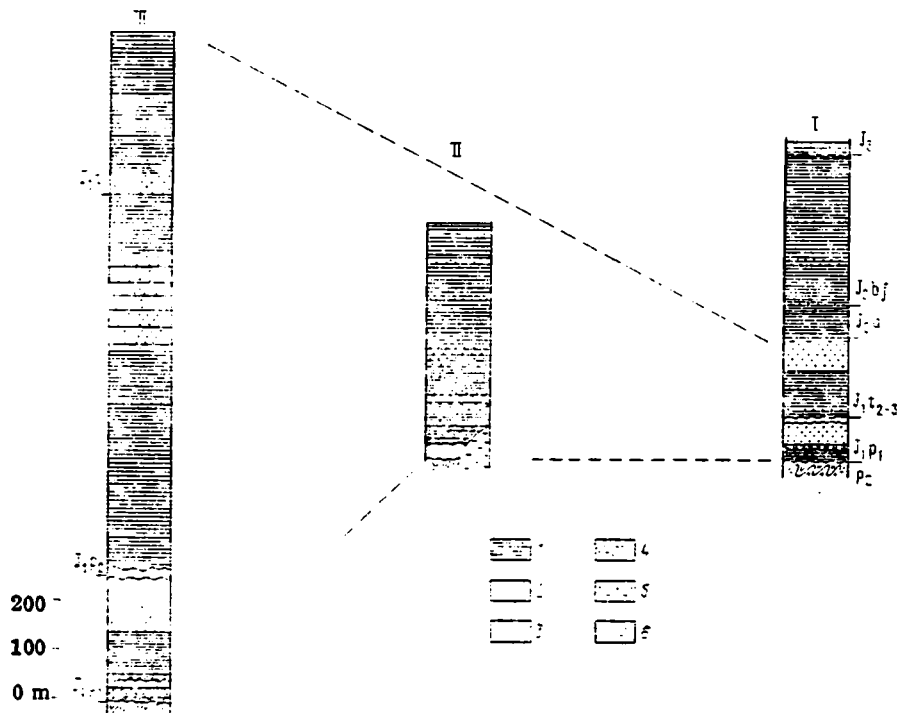


Fig. 2. Correlation of the sections (I - Labino-Malka zone; II - Tyrnyauz-Pshekish zone; III - Kyrtyk depression): (1) argillite and clay schist; (2) sandstone; (3) conglomerate; (4) dislocated rocks of pre-Jurassic basement; (5) granitoid of El'dzhurta massif; (6) limestone.

pression exhibits a greater stratigraphic completeness than does the section in the Labino-Malka zone.

The bottom portion of the Lower Pliensbachian bed was apparently accumulated in continental environments; the upper part of the section was deposited in a sea basin but close to the shore.

The Mukulan suite, widespread in the Tyrnyauz-Pshekish suture zone, consists largely of the same set of sedimentary rocks as the neighboring sections. At the bottom, sandstone and conglomerate are predominant, with clay members playing a secondary role. Sandstones are coarse- and medium-grained with unclear stratification. Schists are dark gray or black with indistinct stratification and imprints of plant stems and leaves on bedding planes, usually replaced by micaceous minerals. Abundant andalusitic mineralization is observed in these schists (Fig. 4). All crystals of andalusite and, more specifically, its chialstolite variety, contain coaly and clayey grains trapped during crystal growth; the grains appear in an arrangement forming a dark cross (Fig. 5).

At the top of the section, clayey and clay-silty members are predominant; there are also members with interstratified clay slates and sandstones, which sometimes become flyschoid. Sandstones consist of small-grained material. Clayey slates contain a small number of nodules.

Mukulan suite sediments are distributed unevenly: in certain localities they are broken by numerous rupture faults and crumpled, while in others they display a calm course.

Middle Liassic fauna has been found in this suite [17]. On the basis of the structure of the section and its tectonic position and a comparison of the bed structure with the neighboring sections of the same structural-facies zone (Kestantin depression) [15], the lower sand-conglomerate part of the suite can be assigned to the Middle Liassic and the upper largely clayey part to the Lower Toarcian (the Lower Gizhgiz layers).

DISTRIBUTION OF CLAY MINERALS IN THE SECTIONS OF VARIOUS STRUCTURAL-FACIES ZONES

The main mineral of the clay sediments of the Khumarin suite in the Labino-Malka zone is kaolinite. Powder patterns display poor resolution of three-dimensional reflections (027, 117, 207, 137). This may indicate a poor three-dimensional ordering of kaolinite. In minor amounts, finely dispersed Al-Mg-mica 2M₁, practically free of swelling layers, is present in the clay sediments; traces of chlorites are also recorded (see Fig. 3).

In higher layers of the section (the Lower Gizhgiz layers of the Dzhigiat suite), clay sediments contain hydromica-kaolinitic and hydromica-chloritic associations. Kaolinite is common in the lower part of the bed and is superseded by Fe-Mg-chlorite (see Fig. 3) at the bed top; the parameter *b* of this chlorite is 9.22-9.24 Å. The powder patterns of oriented natural preparations register a nearly integer series of basal reflections 00 ℓ with *d*(001) = 10 Å, which corresponds to micaceous minerals. After ethyleneglycol treatment, the first basal reflection is shifted to 9.84-9.80 Å (see Fig. 3), which, according to [14], indicates the presence of 15-20% of swelling packets in the mineral structure. The electron diffraction patterns of oblique structures (EOS) of hydromicas register fairly distinct reflections with *k* = 3*n*, but reflections with *k* ≠ 3*n* are usually not discrete and either merged into a diffuse background or have modulations of this background, indicating a poor three-dimensional ordering of micaceous minerals (polytype modification 1Md-1M).

Argillite of the Baksan layers consist of hydromica, which is virtually identical to the underlying Dzhigiat suite rocks and chlorite. Kaolinite occurs as a minor impurity. In some of the specimens on the interval tending toward the iron ore horizons [6], chlorite is the main component in argillites (see Fig. 3). Chlorite also forms oolites, which contribute to several thin iron ore beds. Inside the argillite strata that contain iron ore horizons, chlorites are represented by high-Fe varieties with *b* equal to 9.30-9.32 Å. According to x-ray powder patterns and electron powder patterns, Fe-chlorite of polytype modification 1b is identified in the oolites.

Clay sediments of the Dzhorsk suite are represented by an association of dioctahedral mica (Fe-Mg-chlorite) with a minor content of kaolinite. Based on electron diffraction data, hydromica consists of a mix of polytype modifications 2M₁ and 1Md. Describing the polytype pattern of chlorites is difficult because of a substantial presence of the micaceous mineral. In some of the specimens, however, Fe-Mg-chlorite 1b with the parameter *b* of 9.22-9.24 Å can be identified.

As seen from Fig. 3, the distribution of clay minerals in the section is uneven. At the bottom of the bed, kaolinite is the main rock-forming mineral; in higher horizons it appears as an impurity. Fe-Mg-chlorite supersedes kaolinite in the middle and upper portions of the section; in the zone of iron ore beds it becomes highly ferruginous. Dioctahedral micaceous minerals are present throughout the section in various amounts. While in Khumarin suite fine-

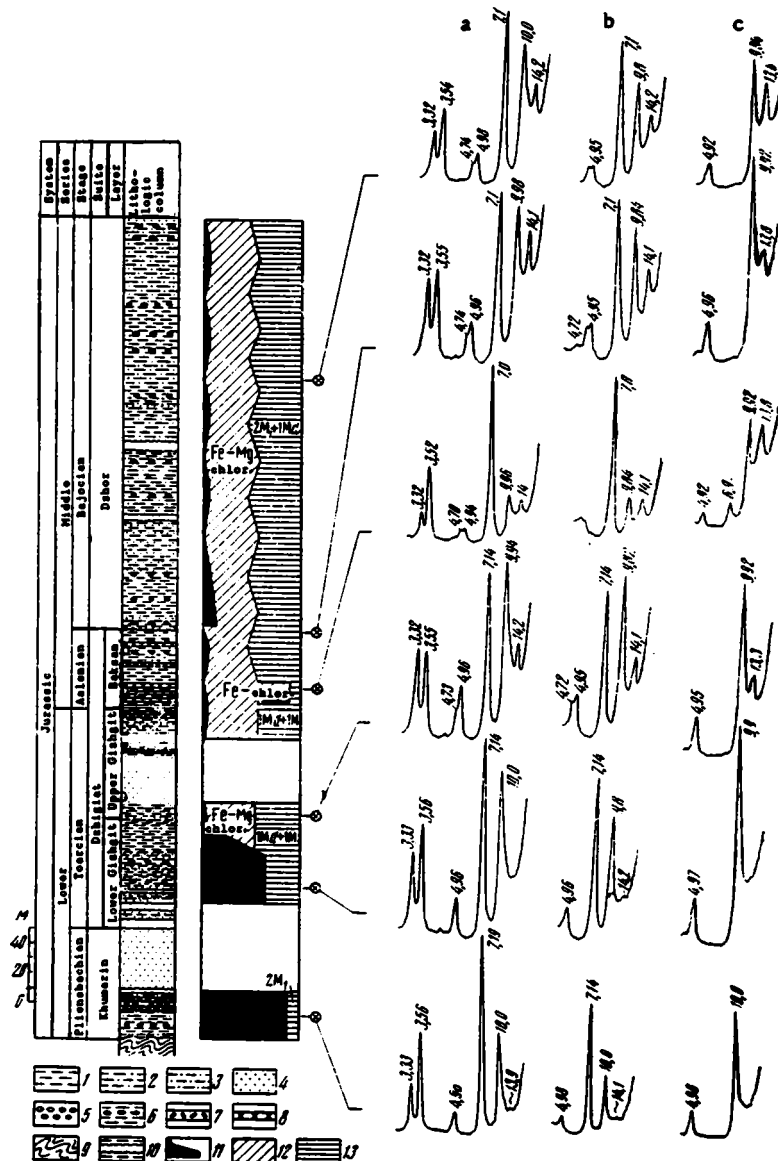


Fig. 3. Lithologic-stratigraphic column of Labino-Malka zone; distribution and diffractograms of clay mineral preparations: (1) argillite; (2) silty argillite; (3) siltstone; (4) sandstone; (5) conglomerate; (6) nodules; (7) beds of nodular conglomerates; (8) iron ore horizons; (9) pre-Jurassic basement rocks; (10) closed intervals; (11) kaolinite; (12) chlorite; (13) hydromica. Specimens: (a) natural air-day; (b) treated with ethyleneglycol; (c) heated to 550°C.

ly dispersed dioctahedral mica $2M_1$ is diagnosed, the Dzhihiat suite contains poorly crystallized hydromica $1Md-1M$, and Dzhorzhinsk suite $2M_1$ and $1Md$. The proportion of swelling layers in these hydromicas ranges from 15 to 20%.

The Kyrtyk Depression

Dioctahedral hydromica-kaolinite associations with an approximately equal ratio of the minerals (Fig. 6, specimen 894) is typical for the Lower Pliensbachian of the section, as well as for the contemporaneous rocks of the Labino-Malkan zone. According to x-ray powder patterns, hydromicas contain up to 15-20% of swelling layers. Electron patterns showed the hydromicas to be poorly crystallized varieties of polytype modifications $1Md > 2M_1$. Up the section, the Upper Pliensbachian and Toarcian contain both hydromica-kaolinitic associations and hydromica-

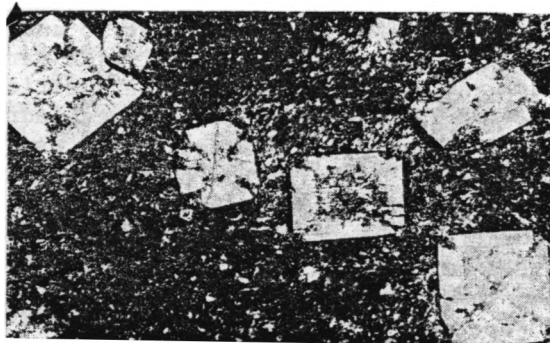


Fig. 4

Fig. 4. Clayey schists, Mukulan suite, with andalusite (chiastolite) inclusions; polished section, magnification $\times 30$.

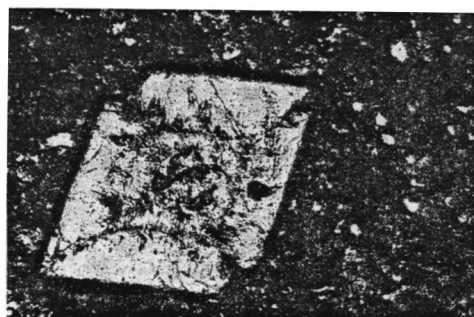


Fig. 5

Fig. 5. Andalusite (chiastolite) crystal with small inclusions of coaly and clayey material; magnification $\times 100$.

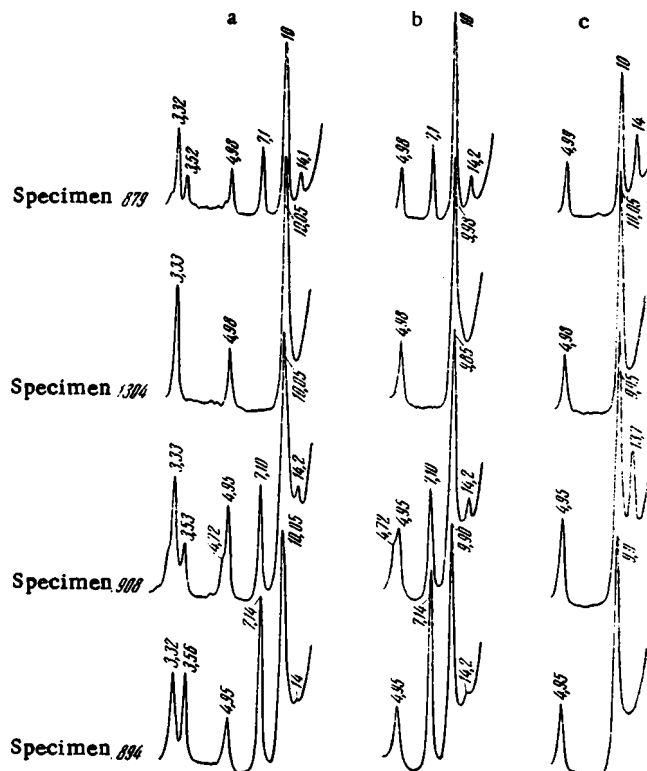


Fig. 6. Diffractograms of oriented preparations. Specimens: (a) natural air-dry; (b) treated with ethylene-glycol; (c) heated to 550°C .

Fe-Mg-chlorite associations ($b = 9.22\text{--}9.24 \text{ \AA}$) (Fig. 6, specimen 908). Dioctahedral mica minerals consist of a mix of polytype modifications $2M_1$ and $1M_d$ in comparable proportions.

Mukulan Suite

Unlike the Labino-Malkin zone and the Kyrtyk depression, the clay schists of the Mukulan suite experience a succession of mineral associations. At the bottom of the bed outside the hornblendization zone, in the clay rocks, which contain abundant segregations of andalusite crystals (Figs. 4 and 5), only dioctahedral mica is present (see Fig. 6, specimen 1304). X-ray powder patterns of this mica show it to be practically free of swelling layers. Electron diffraction studies were done on three specimens of this mica. The patterns were identical. EOS record the complete set of distinct three-dimensional reflections $hk\bar{l}$, both with $k = 3n$

and $k \neq 3n$, indicating a high degree of three-dimensional ordering. A geometric analysis of the positions of reflections showed this mica to have a monoclinic unit cell with parameters $a = 5.19 \text{ \AA}$, $b = 8.99 \text{ \AA}$; $c = 10.12 \text{ \AA}$, $\beta = 100.3^\circ$. The distributions of the intensities of the reflections 02 $\bar{2}$, 11 $\bar{2}$ ($k \neq 3n$), however are sharply different from those in dioctahedral micas 1M. Micas 1M with a vacant transoctahedral position in the first ellipse of EOS usually have the strongest reflections 11 $\bar{2}$ and 112 with medium 02 $\bar{2}$ and 113. In this case an equalization of the intensities of reflections 02 $\bar{2}$ and 11 $\bar{2}$ was observed (Fig. 7). Such distribution is characteristic for 3T micas, but in that case the ratio $(c \cos \beta)/a = 1/2$, when indicating the diffraction spectrum of mica in one-layer monoclinic unit cells. For this mica, however, the ratio was 0.35. Data reported in [20, 21] suggest that the changes in the distribution of intensity of the reflections 02 $\bar{2}$ and 11 $\bar{2}$ ($k \neq 3n$) are due to a redistribution of octahedral cations in dioctahedral 2:1 layer silicates. In particular, the "evening" of the intensities of reflections 02 $\bar{2}$ and 11 $\bar{2}$ and a decreased monoclinicity angle β are due to an equiprobable distribution of octacations among the available cis- and transoctahedral positions. In dioctahedral smectite minerals, various alternative distributions of octahedral cations are possible: from a structure with vacant transposition, to a structure with equiprobable distribution of octacations, to structures with populated transpositions [21, 23]. For dioctahedral micas 1M, however, no minerals have been diagnosed, to our knowledge, with an equiprobable distribution of cations among available octahedral positions.

At the section top, a change of the mineral composition occurs. Sericite 2M $_1$ -chlorite associations are widespread here (see Fig. 6, specimen 879). The mica 2M $_1$ exhibits a high degree of structural perfection. Besides Fe-Mg-chlorite, its more ferruginous variety appears in the section.

FORMATION OF THE ASSOCIATION OF CLAY MINERALS

The present picture of the mineral composition of the sediments was formed under the action of numerous factors, including various sources of material and environments of sedimentation, diagenesis, and postdiagenetic processes. Clay minerals responded with a high sensitivity to the facies of sedimentation. This is reflected graphically in the mineral composition of clay rocks from the Labino-Malka zone.

As mentioned before, kaolinite is the leading component of argillites from the Khumarin suite. The impact of the environment on clay formation was particularly strong in these sediments. From certain features of the geochemical pattern of Khumarin argillites it is possible to reconstruct the conditions in lake-swamp sediments of the early Pliensbachian. These rocks are enriched in C $_{org}$, with amounts of up to 3-9%, and depleted of Fe (0.8%), Mn, Ca, Mg, and Na, i.e., most cations [6]. On the other hand, argillites contain layers of nodules and lens-shaped beds consisting of siderite, which includes Mg, Mn, and Ca as an isomorphic or mineral impurity. Obviously, the primary matter concentrated in nodules was originally dispersed throughout the sediment, increasing the concentration of cations in it. Their redistribution occurred during the course of a diagenetic alteration. The high content of vegetable organic matter (OM) facilitated this process. As OM decayed, CO $_2$ and organic acids accumulated in the ooze, producing an acid medium - a phenomenon described in existing continental water basins of this type [9]. As a result, iron-containing terrigenous minerals (primarily chlorite) were decayed and released Fe and several other cations; as these were redistributed, they took part in the formation of the nodules or diffused into bottom water and were removed from the sediment. The process created conditions for enriching ooze with silica and alumina, so that a favorable setting was created for authigenic kaolinite to develop. In Khumarin argillites a minor chlorite admixture is present; it seems to be a residue of a larger quantity of the mineral in the original sediment. Studies of existing sediments support the geochemical reconstructions of the ancient strata. The decay of terrigenous components during the Quaternary has been studied by Timofeev and Bogolyubova [18]. They showed that in peat bogs of Rioni trench, in subsiding sediments with an acid environment, montmorillonite and chlorite disappear gradually, while kaolinite content rises; sometimes, free silica appears, formed as a result of decay of silicate minerals.

Khumarin argillites are distinguished from the rest of the section by the fact that 2M $_1$ micas with no swelling packets are found in them. Lake-swamp sediments here were formed by accumulation of decay products of the pre-Jurassic basement and their nearby redeposition. The limited migration and rapid burial provided a good preservation of the mica.

With the beginning of the Middle Toarcian there was a northward transgression of the sea, which flooded extensive tracts of the southern Scythian platform, forming Dzhigiat suite sediments. At the beginning of that stage, sand-clay sediments accumulated in a near-shore environment: the material brought here consisted mainly of erosion products from previous continental formations, particularly crusts of weathering that developed in the pre-Toarcian time [4]. In the near-shore sediments that were high in OM, diagenetic processes developed vigorously, giving rise to large amounts of siderite and its associated kaolinite. Authigenic kaolinite of marine sediments combined with that brought from the land to enrich the lower horizons of the Dzhigiat suite. Since the crystalline schists of the pre-Jurassic basement reworked by metamorphic processes had no kaolinite, its formation on land is attributed to Jurassic continental lithogenesis.

As the transgression continued and the shoreline moved farther away from the location, the sedimentation setting in the basin became different; the amount of kaolinite in sediments dropped, and by the end of the Lower Gizhgit time it was replaced almost fully by chlorite (see Fig. 3). Some kaolinite, however, is registered almost throughout the Lower and Middle Jurassic sections. It is possible that considerable amounts of the material were brought into the water basin, but in an open shelf with active hydrodynamics and sediment rewashing it was unstable.

The development of the new hydromica-chlorite associations was a result of new sources of material becoming involved in the process as well as changed sedimentation conditions; the importance of the eroded sources changed in time. This is indicated, in particular, by the distribution of chlorite in the Dzhigiat suite. While generally Fe-Mg-chlorite is prevalent in the sediments, highly ferruginous chlorite, both allogenic and authigenic, mainly enriched clay sediments during the Aalenian time, when iron ore horizons were formed as a result of erosion of the crusts of weathering of Malka serpentinite massif. In the oolites, made of high-Fe chlorite, the polytype modification Ib has been determined, which is typical for sediments formed in subsurface conditions of the sedimentary cover [22]. As one moves away from the high-Fe interval in the section, the chlorites become Fe-Mg-chlorites; judging by some data, they could also belong to the polytype modification Ib. This chlorite variety was also characteristic for Bajocian basin sediments.

The relationship of authigenic and allogenic sedimentary components is an important question in reconstructing the development of clay mineral associations and their features. It is hard to answer this question for the entire strata. In certain horizons, however, one can speak with confidence of the presence of authigenic formations. This refers especially to the clay member at the base of the Khumarin suite, where we believe large amounts of mainly authigenic kaolinite to be present as well as terrigenous mica. Kaolinite at the base of the Toarcian bed is partly authigenic. Well-crystallized authigenic kaolinites have been found in Septarian cracks of siderite nodules from the top of the Lower Gizhgit layers; the surrounding argillites consists of hydromica and chlorite.

Another interval where diagenetic processes were active is the lower half of the Baksan layers, which contains iron ore horizons.

Ferruginous chlorites from well-preserved oolites forming rare and thin (0.1-0.2 m) beds are authigenic, unlike hydrogoethitic oolites, obviously brought in from the Malka massif. Some of the chlorite from argillites, especially in high-Fe intervals, is clearly diagenetic, as well as the chlorite that forms oolites. Yet, chlorite and hydromica grains among the silt admixture in the rock indicate an important role of allogenic material in the fine fraction.

That material from land was the principal factor in the development of clay beds is supported by the alterations experienced by mica minerals. Hydromica 1Md (and 1M) is predominant in the Dzhigiat suite, but at the transition to the Dzhor suite a large presence of polytype modification 2M₁ is observed. This reflects a restructuring in the sources of material supply in the north and the introduction during the Bajocian of new sources in the south due to erosion of the rocks of the Caucasus islands. New sources of materials are indicated also by analysis of the mineral composition of heavy fractions of sand-silt rocks [3]: in the Early Toarcian-Aalenian a sphene-rutile-tourmaline-zircon-chlorite (chlorite in the Aalenian) association is common, while during the Bajocian it is superseded by a zircon-chlorite-biotite-garnet association.

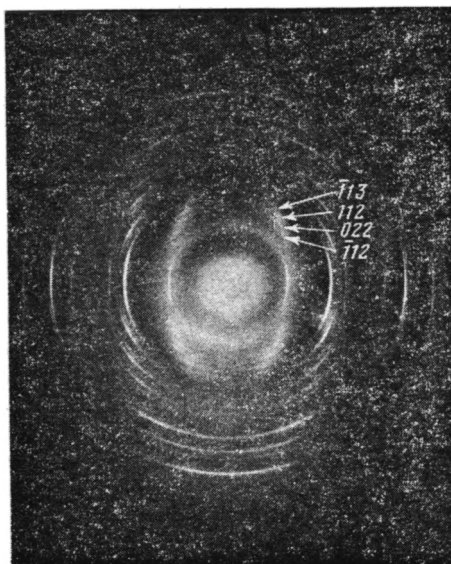


Fig. 7. Electron pattern of a preparation of mica, polytype modification 1M, with equiprobable distribution of octacations.

Within the denudation region, basement rocks were mostly widespread in the Jurassic — crystalline schists, granitoids, etc. — and continental formations from the pre-Jurassic and Early Jurassic, represented by terrigenous and volcanogenic rocks. In view of the limited development of continental sediments in the region, it is possible that by the beginning of the Toarcian transgression they were largely eroded (especially the Upper Pliensbachian and Lower Toarcian), increasing the relative proportion of rocks from the pre-Jurassic basement in the material supplied.

Micas of the polytype modification 2M₁ are typical for metamorphosed pre-Jurassic rocks. Similar micas are observed in Khumarin argillites that accumulated in continental basins. In the marine Toarcian-Aalenian sediments, however, mica 1Md is predominant, while in the Bajocian beds it is present in equal proportion to 2M₁. Some of the 1Md mica could be formed from the material of volcanogenic strata (Shoansk suite, Upper Pliensbachian) by a consecutive formation of montmorillonite-mixed layer mineral-hydromica. The bulk of clay minerals, however, was produced by a reworking of the decaying pre-Jurassic basement.

For estimating the real possibilities of the reworking of material with 2M₁ in an actual geological environment, we investigated the suspended matter from a mountain river which grains the area of slates that contain exclusively the mica 2M₁ and chlorite [7]. The study was conducted on one of the sources of the Avar Koisu River in Dagestan — the Sara-or River, which is approximately 8 km long. At its upper reaches the river flows through bedrocks and at the middle and lower reaches over alluvium; the river in the lower reaches is 5–8 m wide. The suspended matter was collected near the river mouth after a rainfall. X-ray powder patterns and electron patterns of the clay fraction indicated a presence of micaceous mineral 1Md and kaolinite as an impurity in addition to chlorite and 2M₁ mica typical for bedrocks of the catchment area. These components of the suspended material were formed as a result of destruction of bedrock, its transport by the river, deposition in the alluvium and its rewashing, and also in soil developed on the alluvium on mountain slopes. We are concerned here with the final composition of the suspended matter carried downstream rather than the dynamics of alteration or formation of clay minerals. Importantly, a sharply articulated alpine relief is observed in the river basin; the stream is a typical mountain river with a high rate of denudation processes. New components in the eroded material were thus formed rather rapidly.

The relative speed (in the geological time frame) of the development of 1Md hydromica in Recent times supports the theory that at least a mix of 1Md and 2M₁ was brought into the water basin during the Jurassic. The accumulation of the material on the shelf and its repeated rewashing and redeposition, however, caused 1Md hydromica to become predominant in some of the intervals (Dzhigiat suite).

In the Kyrtyk depression, where the sediments are indicative of the sedimentation environments within the northern slope of the geosynclinal trough, the Pliensbachian and the Toarcian were the times of stable marine sediment accumulation (except for the basal horizon), while the eastern Labino-Malka zone until and through the early Toarcian remained elevated and supplied material into the basin. As a result, the lower part of this section in the Kyrtyk depression has the typical traits of the redeposition of products of continental accumulations (conglomerate lenses, numerous imprints of leaves and stems of land plants, etc.). The hydromica-kaolinitic association is connected with this bed. Unlike Khumarin argillites, which contain 2M₁ mica, hydromica 1Md and 2M₁ are common here; swelling layers account for 20%, i.e., a substantial quantity of 1Md hydromica was introduced during the rewashing and redeposition of material from land. As the micas decayed, the proportion of swelling layers increased.

In the Upper Toarcian part of the Kyrtyk section, a hydromica-chloritic association is widespread, though in some of the intervals chlorite is replaced by kaolinite. This change occurs without any visible lithological alteration.

Variations in mineral distribution of this kind can be due to different sources of material eroded in the northern part of the shore, the rewashing and redeposition of littoral sediments on the shelf, and probably sporadic downwash of material from islands which developed near the Tyrnyauz-Pshekish zone. Comparing the Kyrtyk depression profile with the contemporaneous portion of this section of the Labino-Malka zone, we see similarities in the distribution of clay mineral associations: the bottom parts of the strata are enriched in kaolinite, while in higher horizons chlorite appears, and in marine sediments 1Md and 2M₁ hydromicas with swelling packets of 15-20% are present. These features of mineral composition and distribution of clay material should be taken into consideration in studies of the formation and alteration environments of clay components of the Mukulan suite.

The rocks of this suite were substantially altered during the postdiagenetic stage, and their original composition has been changed greatly. It is important to estimate the probable primary composition of these sediments, so as to describe the type and direction of their alterations.

Since this suite occurs between two other sections studied and has common structural features with them, there are grounds to assume that the original mineral compositions of clays in the Mukulan suite section (Tyrnyauz-Pshekish suture zone) and the sections adjacent to it in the Labino-Malka zone and Kyrtyk depression were identical.

The sediments in all three sections sank to about the same depth of approximately 2 km. The degree of alteration of the sediments, however, was not the same. A relatively greater dislocation of Mukulan layers is due to the mobility of this zone — the displacements along large faults which caused smaller disruptions and local crumpling of layers. The rocks, however, were not subjected to any intense stress; no widespread cleavage is observed. The pressure factor does not seem to have played a major role in the alteration of Mukulan rocks.

Another potential strong alteration factor is temperature. Heat carriers — all kinds of intrusive bodies of various morphology and composition — are common in this region within the Tyrnyauz-Pshekish suture zone. The Mukulan sediments in the eastern part of the territory are in contact with a major intrusion of El'dzhurta granites. Exploratory drilling [17] indicates that, at some depths, this massif exerted a thermal action upon Mukulan rocks. Other intrusive bodies that did not directly cut across clay schists were apparently also active heat carriers, generating a substantial heat flow in the area.

Comparing the composition of the clay rocks of the Mukulan suite with the sediments of adjacent sections allows estimating the direction of the alterations that occurred in these rocks (Fig. 8). In the bottom parts of the sections the kaolinite (main phase)-hydromica association in the Kyrtyk depression is succeeded by an association of dioctahedral mica 1M with equiprobable distribution of octahedral cations and andalusite. The similarities of the chemical compositions of minerals such as kaolinite $\text{Si}_2\text{Al}_2\text{O}_5(\text{OH})_4$ and andalusite Al_2SiO_5 are remarkable. Since kaolinite has a relatively low resistance to an increase of P-T characteristics, one can assume with some confidence that in the environment of rising temperatures the decay of kaolinite yielded ingredients that crystallized as a higher-temperature mineral. The fact that the process occurred at a depth of at most 2 km and the temperature was beneath 500°C determined that, of the three possible polymorphic modifications of the Al_2SiO_5 system, andalusite that formed (rather than disthene, which is the high-pressure variety, or sillimanite, which is the high-temperature variety).

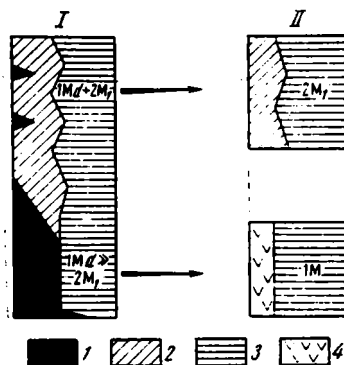


Fig. 8. Distribution of clay minerals in Lower Jurassic of the Labino-Malka zone and Kyrtyk depression (I) and Mukulan suite of the Tyrnyauz-Pshekish zone (II): (1) kaolinite; (2) chlorite; (3) mica minerals; (4) andalusite.

The replacement of a layer silicate mineral by a mineral from island silicates suggests that andalusite was formed by synthesis.

Andalusite is a typical mineral of the facies of contact and regional metamorphism and is indeed found in hornblende from Tyrnyauz intrusions. The andalusite schists studied by us, however, are outside the zone of rock hornblendization. These schists seem to have been reworked in conditions of late catagenesis-metagenesis: they retain residual traits of sedimentary textures, and the rocks cleave along directions coincident with or similar to the layering.

In discussing the formation of the mica we should bear in mind that, originally, an admixture of hydromica $1M_d \gg 2M_1$, containing up to 20% of swelling layers was present in the sediments, as well as kaolinite. As a result of alterations, $1M$ mica appeared within an equiprobable distribution of octahedral cations among available positions in its 2:1 layers. The most probable theory is that this mica is neomorphous. To our knowledge, no similar mica has been described in the literature. In some experiments muscovite has been synthesized from kaolinite, yielding only $1M$ mica [10]. The authors of [10], however, did not describe the cation distribution in the structure of the mica synthesized.

The lithological top of the Mukulan suite bears no traces of redeposition of continental sediments. Judging by its appearance, it is a marine bed. The $2M_1$ mica-chlorite associations are common here. On the other hand, in the contemporaneous beds of the Kyrtyk depression, mainly $1M_d-2M_1$ hydromica-chlorite association is observed, with a subordinate quantity of kaolinite (see Fig. 6, specimen 879).

Swelling layers disappear in the upper part of the Mukulan suite from micaceous minerals, the mix of polytype modifications $1M_d$ and $2M_1$ is superseded by $2M_1$ mica alone, and a high-Fe variety appears in addition to the Fe-Mg-chlorite. That this part of the bed was also affected strongly by heat is evidenced also by the local hornblendization zone, mainly near the edge of the strip where the rocks of the suite are found.

One possible theory for the processes in these sediments can be based on an experimental investigation. In [12] the basic possibility was shown experimentally of a polytype transformation of $1M$ muscovite into $2M_1$ at high temperatures. The authors described the transition as the evolution of two consecutive reactions — dissolution and crystallization.

We thus see diverse mineral associations in the different parts of the Mukulan suite. Three facts should be considered in discussing the possible conditions in which they were formed. First, the leading role of the temperature in rock alteration is quite obvious, because the adjacent sections that subsided to the same depth and were subjected to the same geostatic pressure exhibit different features of clay minerals; despite the dislocation of the beds, the rocks bear no tangible signs of lateral stress. Secondly, since the strip in which the rocks of the suite occur stretches for almost 4 km, the thermal processing of this bed and the probable action of fluids and gas emanations were different in different parts. These differences could be to some extent responsible for the specifics of mineral formation. Thirdly, a leading factor which produced the different mineral associations in the Mukulan

strata due to thermal metamorphogenic processes was the primary composition of rocks that took shape during the early sedimentogenesis and diagenesis.

The dating of the alteration of Mukulan rocks depends on the main heat carrier. The age of the biotite granitoids of the Él'dzhurta massif has been estimated as 2 [5] or 3.31 million years [1]. Leucocratic granites are older (about 20 million years). Metallization of Tyrnyauz time is at least 20 million years [1]. All the processes of ore and granite formation were accompanied by a heightened heat flow and must have contributed to metamorphism of the Mukulan bed. One should hardly expect to be able to narrow this time interval significantly. The relatively young age of Él'dzhurta granites was determined from a finely shaped body. The evolution of granite massifs according to some data, however, may span several (5 to 10) million years [8]. We believe that the main alterations of sand-clay beds occurred during such a "preliminary" stage — before the granite intrusion was formed. This is supported by the data of investigators who determined that hornblendization zones tending spatially to the Él'dzhurta massif were formed before the intrusion of granite magma [11, 13, 19]. The development of new associations of clay minerals in Mukulan schists and andalusite mineralization (beyond the hornblende areas), and the time during which high temperatures acted upon rocks, was quite long, as indicated, in particular, by the presence of well-shaped and relatively large (5–8 mm) acicular andalusite crystals.

An analysis of the influence of heat on the alteration of clay rocks helps describe the specific evolution of catagenetic and metagenetic processes in locations with different heat flow regimes. The results of these studies, combined with facies analysis, will make it possible to come closer to paleolithological reconstructions of deeply altered clay-schist rocks in other regions as well as the Caucasus.

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SUPERGENE PHOSPHORITE ORES IN THE BUKANTAU MOUNTAINS (NORTHERN KYZYL KUMS)

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Supergene phosphorites and phosphate rocks discovered for the first time by the author in the Bukantau Mountains (Northern Kyzyl Kums) are described. Their composition, ore content, and genesis are shown to be similar to phosphorite deposits of the Karatau.

Following the discovery in 1936 of a vast phosphorite basin in the Lower Paleozoic of the Lesser Karatau (Southern Kazakhstan) some investigators turned their attention to the possibility of discovering such deposits in neighboring regions where similar formations were known. A potential site of Lower Paleozoic phosphorites was the Lower Paleozoic black shale, predominantly siliceous formation interlayered with carbonate and aluminosilicate rocks, developed in the Nurata Mountains and on Paleozoic highlands of the Kyzyl Kums [10, 16].

Extensive geological studies begun in the Kyzyl Kums in the second half of the 1950s and culminating in the discovery of a number of minerals contributed greatly to the stratigraphy, lithology, and paleogeography of black shale deposits. Among them were distinguished at least two uneven-aged formations, separated everywhere by carbonate, well-dated fossil remains and by Devonian and Lower Carboniferous (C_{1v}) deposits.

Among black shale formations underlying Devonian carbonate rocks most investigators distinguish today the Auminzatau (PR₁₋₂), Taskazganskaya (PR₃), and the Besapanskaya (S-D₁) suites [17]. Overlying the Visean limestones is also a black shale Karashakhskaya Suite of the Middle Carboniferous, composed of carbonaceous-siliceous-clay shales with lenses and interlayers of carbonate rocks.

In the course of routine and specialized phosphorite research of black shale formations discoveries were made in the 1950-1970s of phosphorus-rich beds in different regions of the Kyzyl Kums [18-20]. Many of these finds were located in the Bukantau range (Northern Kyzyl

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Kums) [1]. They are also confined here to black shale formations, whose age has yet to be definitely determined and ranges from the Vendian up to and including the Middle Carboniferous [17]. The most complete description of Bukantau phosphorite occurrences is given in [9] and elsewhere. Il'yashenko in the vicinity of the Irlir spring (now a well) traced over a distance of 11 km a formation up to 150 m thick, represented by dolomites interlayered with siliceous-calcareous and carbonaceous-calcareous shales. The content of P_2O_5 in dolomites with cherty inclusions reaches 6%, in carbonaceous-siliceous shales 7% and in siliceous-carbonate rocks varies between 1.89 and 11.08%. Originally the age of this formation was dated by him as Namurian, but most investigators today are inclined to date this phosphorite occurrence as Vendian.

A number of occurrences of phosphate-bearing rocks are known in the west of Bukantau near the Chalkaratau Mountain north of Uchkuduk. Here, according to Il'yashenko, two lenticular interlayers of phosphatized rocks containing between 0.89 and 1.12% P_2O_5 have been found among deposits of the Kokpatas Suite of the Middle Carboniferous. In the same region one of the wells in the 65.5-192.7 m depth range penetrated four interlayers of phosphate rocks 0.2 to 2.15 m thick, containing between 0.94 and 20.44% P_2O_5 .

Phosphatization was discovered also at the center of the Bukantau in the Kokpatas Mountains. Here, 3 km west of the Sautbai well, phosphatized crush zones were found in carbonaceous-siliceous shales, limestones, and dolomites. The content of P_2O_5 here varies between 0.54 and 8.98%.

In the immediate vicinity of the central part of the Kokpatas anticline (7 km north of the Kokpatas well) phosphatization was observed at the base of the Kokpatas Suite among silicified dolomites interlayered with siliceous rocks. The content of P_2O_5 here reaches in places 10.23% in a thickness of phosphate-bearing rocks of 51 m. In the zone of weathering of these rocks Kasymov discovered secondary phosphorus minerals [11].

The "Khimgeolnerud" expedition of the Uzbek Ministry of Geology at the end of the 60s and beginning of the 70s conducted detailed studies of outcrops of phosphatic black shale formations but, failing to find a single prospective ore occurrence, concluded that there were no Paleozoic phosphate deposits in the Kyzyl Kums, and phosphorite research here was discontinued.

Another factor which contributed to the lack of interest in phosphorite research in black shale formations of the Kyzyl Kums was the discovery at the end of the 60s of pelletal phosphorites among Eocene marine deposits bordering the Tamdytau Mountains [3, 8].

As to the possibility of discovering deposits of secondary phosphorites (metasomatic and karst) in the Kyzyl Kums such as those known in the USSR in the Altai-Sayan region, in eastern Sayan, and on the Enisei range or abroad (in Tennessee and Florida) [4-6, 12, 13], such problems were never even discussed. What is more, on the other hand, Rakhimova [18] observed that in the Bukantau Mountains on weathering and leaching of phosphorite deposits the content of P_2O_5 in them decreases sharply. Therefore, "in the presence of a thick weathering crust one cannot be limited merely to a study of surface zones but should be guided by data obtained from a study of rocks at depth" [18, p. 144]. The data available in the literature cause us to disagree with this view.

Supergene (secondary) phosphorites (metasomatic and karst) are known in neighboring regions of the Fergana Basin and Lesser Karatau.

Boiko et al. [2] in studying secondary phosphorites of Fergana associated with Precambrian phosphate rocks assume that a silicite-phosphate breccia, occasionally reaching a thickness of 30 m with an average P_2O_5 content of 15%, forms in the weathering crust. This breccia is composed of acute-angled fragments of phosphatic Lydian stones ranging in size from fractions of a millimeter to 0.5 m, cemented with light gray pelitomorphous phosphate.

In the Lesser Karatau the processes of karst formation occur directly on phosphorite deposits, at the contact of Proterozoic dolomites and siliceous phosphorites. Depressions 10-20 m deep are distinguished in the walls of the Zhanatas quarry. They are filled with yellowish white loose clay or compact porcelainlike formations containing 30-40% P_2O_5 [7].

In the course of field work in 1984-1986 on study of the ore-bearing weathering crust and eluvial-karst placers of ultraheavy minerals we discovered for the first time in the Kokpatas Mountains (south-facing slopes of the Bukantau range) high-grade phosphorite ores of fundamentally different age and genesis than those known here earlier (Fig. 1) [14, 15].

The area of prospective ore occurrence known as "Karstovoe" is a large brachyanticline complicated by tectonic deformations of different order. The core of the brachyanticline is composed of Visean limestones (Dzhuskuduk Suite C₁v₃dk); the limbs are composed of a thick, faunistically uncharacteristic formation of weakly metamorphosed sedimentary and volcanic rocks of the Karashakhskaya Suite provisionally dated as Middle Carboniferous.

Deposits of the Dzhuskuduk Suite are gray, light-gray massive limestones interlayered with detrital carbonate rocks. In the roof of this formation are rocks enriched in clay material. At the contact of detrital and massive limestones in the western part of the carbonate limb of the brachyanticline is a thin (up to 3 m) discontinuous horizon of bauxites. The latter form small lenticular granular bodies and presumably fill the network of karst depressions along crush zones of the rocks. The age of the limestones according to numerous fossil assemblages (brachiopods, corals, foraminifera, etc.) is dated as late Visean [17]. The thickness of the suite exceeds 300 m.

The Karashakhskaya Suite (i.e., the black shale formation overlying carbonate rocks C₁v) is represented by volcanic rocks (diabases, porphyrites, tuff breccias, and lava breccias) interlayered with terrigenous rocks (gritstones, carbonaceous-siliceous and carbonaceous-clay shales, and sandstones), which occur roughly in equal proportions. In the roof of these beds are occasionally found lenticular interlayers of carbonate rocks up to 40 m thick. The thickness of the suite reaches 750 m.

Intrusive formations in the region are extensive and are arbitrarily classified into three uneven-aged groups. The earliest group is the ultrabasic, basic, and acidic igneous rocks, which, like the enclosing formation, have undergone regional metamorphism. The second group of intrusive formations is represented by granitoid rocks, which comprise the large Kokpatas massif, and by associated dikes of aplites and pegmatites.

The youngest group of intrusive formations is represented by dikes of intermediate and subalkalic (calc-alkalic) composition: diorites, kersantites, diorite-porphyrites, and syenite-porphyries. Most likely the zones of intense metasomatic alteration of carbonaceous shales containing rich pyrite-argentopyrite mineralization are synchronous to these dikes.

Over vast areas of Paleozoic rocks is developed a weathering crust a few meters to tens of meters in thickness. The weathered rocks are overlain in places by poorly cemented conglomerates of the Upper Cretaceous (?).

All outcrops of phosphorite ores documented by us gravitate in one way or another toward the contact zone of carbonate rocks and shales of the Karashakhskaya Suite. Carbonate rocks (predominantly dolomites and dolomitic limestones) within the studied region having a combined area of about 0.2 km² form isolated lenticular outcrops 100-200 m in length. It is possible that these carbonate bodies are organogenic structures, which existed in the shelf zone of a Middle Carboniferous sea.

On shales is developed a hydrogoethite-hydromica-kaolinite weathering profile, presently complicated under hot dry climatic conditions by a thick superimposed gypsum-carbonate mineralization. Along carbonate rocks in the zone of contact with shales are formed karst cones filled both with residual products of eluvium of terrigenous rocks and with accumulative products of carbonate leaching. It is in these forms of karst relief that the major portion of phosphorite ores is concentrated.

All phosphorites discovered by us can be combined into five groups, differing sharply in composition, structure, and genesis (Table 1).

1. Metasomatic dolomitic-calcareous phosphorites with a patterned structure.
2. Metasomatic siliceous-clayey phosphorites with a fine-grained structure.
3. Dense karst phosphorite breccias (phosphorite collapse breccias).
4. Karst phosphorite nodules and concretions with a brecciated structure.
5. Loose gypsiferous silty clay phosphorite karst deposits.

1. Metasomatic dolomitic-calcareous phosphorites with a patterned structure (Fig. 2) are characterized by the presence of different-colored bands and of various nodules, which are subparallel to the ground surface and which presumably reflect the flow of infiltrating phosphate solutions. The primary appearance of the rock is shaded; only in thin sections are there fragments of primary fine-grained dolomites cemented with fine-grained phosphorite. The walls of the microcracks and cavities in these rocks are filled with radial finely crystalline

TABLE 1. Chemical Composition of Phosphorites and Phosphorite-Bearing Rocks of the Karstovoe Ore Occurrence

Group No.	Sample No.	Rock	Mineral composition, %	P ₂ O ₅	SiO ₂	Al ₂ O ₃	Σ Fe ₂ O ₃	MgO	CaO	Calcium loss	H ₂ O ⁻	H ₂ O ⁺	F	Cl	Impurities, g/metric tons		
															As	Sb	Zn
1	56-5	Metasomatic dolomitic-calcareous phosphorites with a patterned structure	Carbonate fluorapatite 36, dolomite 18, calcite 24, gypsum 7, the rest: hematite, quartz	15,22	2,00	0,25	5,17	3,84	40,10	23,71	1,00	1,50	1,87	0,20	1000	500	2000
	59-5			14,98	Not det.	0,25	5,21	3,92	40,57	24,58	0,38	0,70	1,87	0,26	700	500	700
2	107-6	Metasomatic siliceous-clayey phosphorites with a fine-grained structure	Carbonate fluorapatite 51, kaolinite 16,1, hydromuscovite 12, quartz (opal) 11,4, hydrogoethite 3,6	22,20	25,98	10,02	3,34	0,29	29,23	5,09	Not det.	Not det.	2,09	0,20	670		Not det.
	49-1-85	Dense karst phosphorite breccias	Carbonate fluorapatite 70, quartz 15-20, kaolinite 5-10, the rest: hematite, goethite	28,74	Not det.	4,07	4,46	0,08	40,49	3,00	0,40	1,69	2,90	0,55	200	5000	3000
4	38-1-85			28,47	"	2,14	2,84	0,11	43,33	3,23	0,42	1,24	3,08	0,85	300	2000	700
	77-5	Karst phosphorite nodules and concretions with a brecciated structure	Carbonate fluorapatite 89, the rest: gypsum, calcite, quartz	38,60	1,25	1,06	2,50	Not det.	51,70	2,09	0,20	Not det.	3,00	0,08	1000	500	2000
5	59-4			36,85	Not det.	0,72	0,78	0,06	53,12	2,37	0,41	0,77	3,99	0,55	Not det.	Not det.	Not det.
	49-3-85	Loose gypsiferous silty clay phosphorite karst deposits	Quartz 45-50, gypsum 15-22, carbonate fluorapatite 12-14, kaolinite 2-12, hydrogoethite 10-12	4,64	"	1,53	8,20	0,20	29,28	17,50	2,07	13,30	0,63	0,95	200	5000	3000
6	49-4-85			5,98	"	5,15	9,60	0,34	20,34	11,02	2,35	7,09	0,83	0,50	300	3000	500
	41-4	Clay eluvium after shales	Quartz 57, kaolinite 14, hydromica 14, hydrogoethite 7, the rest: carbonate fluorapatite	0,89	"	12,14	6,14	0,51	2,68	6,77	1,01	3,10	0,20	0,04	700	500	700
7	108-6	Secondary phosphorites (Zhanatas deposit) Lesser Karatau	Not det.	36,84	3,00	0,36	2,00	0,81	52,65	2,41	0,005	Not det.	3,72	0,37	20	Not det.	Not det.

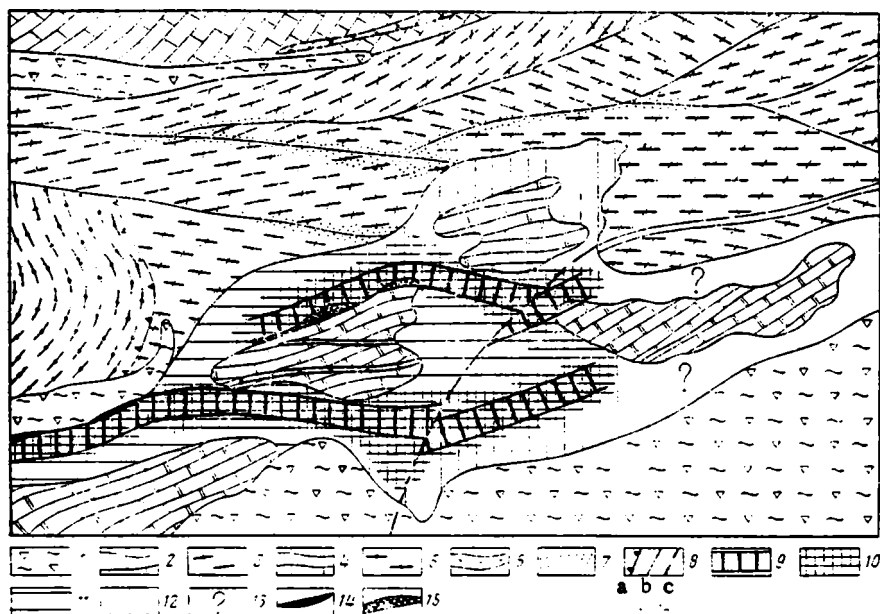


Fig. 1. Geologic schematic representation of the Karstovoe phosphorite ore occurrence (scale 1:2000). 1) proluvial deposits (Q_4); 2) carbonaceous-siliceous shales (C_2); 3) dolomites and limestones of the Karashakhskaya Suite (C_2); 4) limestones of the Dzhuskuduk Suite (C_1V); 5) siliceous shales of the Kokpatas Suite (PR_2); 6) dikes of intermediate and basic composition (PZ_2); 7) zones of intense metasomatism; 8) tectonic deformations (a - thrust, b - fault, c - hypothetical fault); 9) hypothetical zones of occurrence of primary phosphorites in the Karashakhskaya Suite; 10-13) Paleogene-Neogene phosphatic eluvial-karst deposits containing P_2O_5 , %: (10 - >20; 11 - 10-20; 12 - <10; 13 - not sampled); 14-15) outcrops of metasomatically altered phosphorites (14 - siliceous-clay, 15 - dolomitic limestone).

fluorapatite and coarsely crystalline, secondary dolomite and calcite relative to phosphorite. The content of P_2O_5 varies between 14.98 and 15.22%. The absence of silicate detrital material as well as individual relicts of primary rocks suggest that this type of phosphorite could have formed by redistribution of phosphate in primarily dolomitic-calcareous phosphorites.

2. Metasomatic siliceous-clayey phosphorites with a fine-grained structure are hard but cavernous brown rocks with light yellow sinters and thin interbeds. The rock structure is psammitic, in places brecciated. In thin sections the siliceous-clayey phosphorites are fine-grained aggregates of elongated flakes of hydromuscovite and kaolinite embedded in a collo-morphous silica-phosphate cement. There are numerous veinlets filled with fine-grained phosphorite with rims of radial finely crystalline fluorapatite. The content of P_2O_5 reaches 22.2%. This type of phosphorite is possibly a phosphorite metasomatite after primary carbonaceous-siliceous-phosphorite shales.

3. Dense karst phosphorite breccias consist of unrounded commonly coordinated fragments of siliceous, less commonly, clay-siliceous shales, and quartz of different sizes cemented with fine-grained phosphate cement. In addition to phosphate cement there is an appreciable amount of fine terrigenous material represented mainly by quartz and mica. The content of P_2O_5 in phosphorite breccias varies widely depending upon the composition and ratio of cement and detrital material and occasionally reaches 28.47%. These formations are clearly the products of cementation of collapse (founder) breccias.

4. Karst phosphorite nodules and concretions with a brecciated structure up to 1 m in size (average 10-20 cm). Their content in a loose clay-phosphate mass reaches occasionally 50-70% and is on average 20-30%. They differ from phosphorite breccias in that they have little or no detrital material. Such nodules (concretions) vary in shape from oval fragments



Fig. 2. Photograph of a thin section of metasomatically altered dolomitic-calcareous phosphorite (crossed nicols, 12.8 $\times$). A) apatite; K) dolomite, calcite.

TABLE 2. Results of X-Ray Diffraction Studies of Phosphorite Samples, Å

Sample No.	Parameters of the phosphorite elementary nucleus		Accuracy	
	<i>a</i>	<i>c</i>	<i>a</i>	<i>c</i>
49-1-85	9,359	6,890	$\pm 0,003$	$\pm 0,003$
108-6	9,363	6,892	$\pm 0,002$	$\pm 0,002$
59-5	9,356	6,890	$\pm 0,002$	$\pm 0,002$
77-5	9,365	6,890	$\pm 0,002$	$\pm 0,002$
38-1-85	9,358	6,883	$\pm 0,002$	$\pm 0,002$
107-6	9,332	6,892	$\pm 0,002$	$\pm 0,002$

with knobby surfaces to irregular angular fragments. Occasionally they form kidney-shaped protuberances, which overlie dolomitic phosphorites and phosphorite breccias. The nodules and concretions occur most commonly in loose rock, which fills the karst depressions. The structure of these phosphorites is characterized by the presence of pale brownish-orange fragments containing a small mixture of terrigenous material in the fine-grained phosphate. They are cemented with small white crusts of collomorphous phosphate, which is the recrystallized radial formations. The elongated phosphate crystals comprising them are oriented perpendicular to the surface of cracks, cavities, and fragments. The content of P_2O_5 in these phosphorites reaches 38.6% (average 36%).

5. Loose gypsiferous silty clay phosphorite karst deposits are the primary filler of ore-bearing karst depressions. The content of P_2O_5 in them varies widely, reaching in places 5-6%. The composition of the deposits is mainly phosphorite-hydrogoethite-hydromica-kaolinite with a superimposed gypsum-carbonate mineralization.

X-ray studies of a series of samples of different types of phosphorite ores have shown that phosphates of the apatite group are predominant among them. The greater part is represented by a mineral which is distinguished from fluorapatite by lesser values of parameter *a*, which is typical for francolite (Table 2).

Of special note is the high (0.2-0.95%) chlorine content in supergene phosphorites (see Table 1). It would be natural to assume that since ores presently occur in a region with a

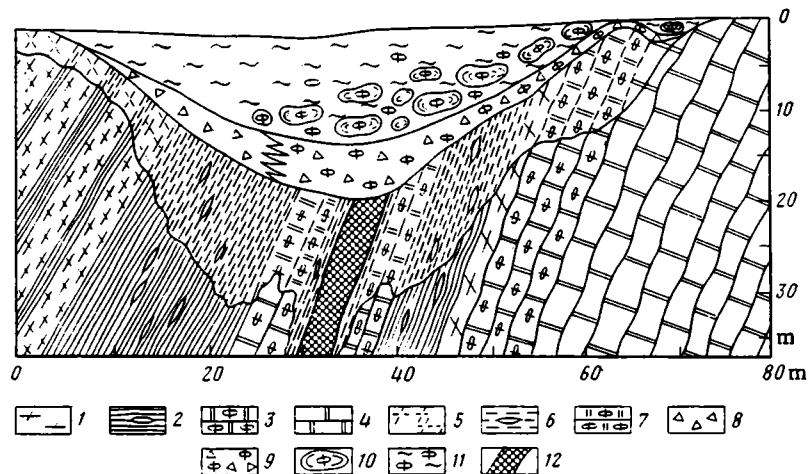


Fig. 3. Hypothetical profile of a phosphorite karst depression of the Karstovoe ore occurrence. 1-7) rocks of the Karashakhskaya Suite (1 - carbonaceous-siliceous shales, 2 - carbonaceous-clay shales, commonly phosphorite, 3 - dolomitic-calcareous phosphorites, 4 - calcareous dolomites, 5 - weathered carbonaceous-siliceous shales, 6 - weathered carbonaceous-clay shales, 7 - metasomatic dolomitic-calcareous phosphorites); 8) collapse breccia; 9) phosphorite collapse breccia; 10) phosphorite concretions in karst deposits; 11) loose phosphorite karst deposits; 12) fault zone.

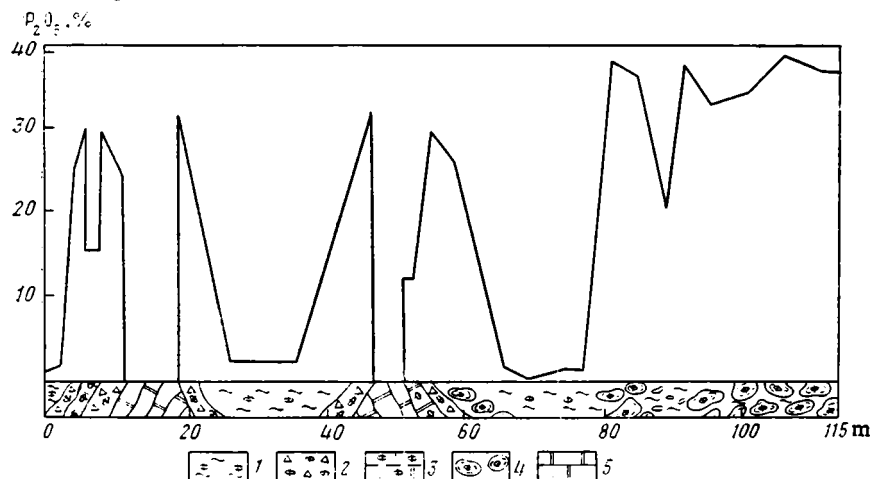


Fig. 4. Profile from one of the trenches at the Karstovoe ore occurrence. 1) Loose phosphorite karst deposits; 2) phosphorite collapse breccia; 3) metasomatic dolomitic-calcareous phosphorites; 4) phosphorite concretions in karst deposits; 5) calcareous dolomites of the Karashakhskaya Suite.

sharply arid desert climate where vast areas are exposed to surface salinization, chlorine in phosphorites should be found in the composition of water-soluble salts. Studies conducted have shown that the content of water-soluble chloride in phosphorites does not exceed 0.005% (i.e., soluble chloride is practically absent). At the same time it does not correlate with parameter α on the x-ray photograph (see Table 2). This fact together with low values of parameter α uncharacteristic of chlorapatite must be very carefully considered before assuming that chlorine enters the apatite lattice. At least the assumption cannot be ruled out.

It is more likely, in our opinion, that chlorine enters into the composition of supergene phosphorites in the form of x-ray amorphous water-insoluble organomineral or inorganic complexes. This is indirectly indicated by the frequent presence of gold in metasomatic phosphorites.

The profile distribution of the above-described groups of phosphorites is shown in Fig. 3. As is evident in Fig. 4 from a hypothetical profile constructed from one of the 1-1.5 m deep trenches, dolomitic phosphorites gravitate toward the contact of carbonaceous-siliceous-clay shales with lenses of dolomitic limestones within the area of development of rocks of the Karashakhskaya Suite (C_2b-m). They are later overlain by dense phosphorite breccias, which most likely pave the floors of karst depressions, unfortunately unexposed by drilling. It is assumed that the thickness of phosphorite breccias will increase toward the center of the floors of the depressions.

Higher in the section of a karst depression is a zone of phosphorite nodules and concretions, which is overlain in the center of ore-bearing karst depressions near the surface by phosphatic clays and siltstones. It should be noted that the broken line of P_2O_5 content along the trench (see Fig. 4) does not reflect the actual position of the bodies, since outcrop deposits are exposed by the trench and phosphorite ores emplaced at a shallow depth most likely occur over considerably large areas.

Unfortunately we have very limited information on the deep structure of phosphorite karst depressions since exploration work in the area was done by pneumatic drilling and phosphorus samples were not analyzed. According to verbal communications of experts who worked here the depth of individual karst cones in the area reached many tens of meters.

Considering such a high phosphorus saturation of the karst formations, it is difficult to imagine that the source of ore could only have been the weakly phosphatized interbeds among deposits of the black shale formation. Comparing the composition of phosphorite karst formations in the vicinity of the Karatau phosphorite deposits with those discovered by us in the Kokpatas ore field (see Table 1), one may conclude that they are similar in composition and degree of saturation of high-grade phosphorites. Such a conclusion suggests that the phosphorite karst of Kokpatas formed at the contact of carbonate and silicate rocks to which beds of ancient (Middle Carboniferous) phosphorite ores of possible economic value are confined.

The basic local criteria of phosphorite research of the types examined are: 1) the contact of carbonate rocks and shales of the Karashakhskaya Suite; and 2) the development along the contact of karst forms filled with phosphorite deposits.

Based on the foregoing the following conclusions can be drawn.

Supergene (metasomatic and karst) phosphorites have been discovered for the first time in the Kyzyl Kums in the Kokpatas Mountains on south-facing slopes of the Bukantau. The content of P_2O_5 in phosphorites varies widely and often reaches 39%.

Phosphorite karst and zones of metasomatic phosphorites are confined to the contact of Middle Carboniferous carbonate rocks and carbonaceous-siliceous shales of the Karashakhskaya Suite. It is assumed that a bed of primary dolomite-phosphorite ore, similar in composition to corresponding varieties of phosphorite ores of the Karatau, may be discovered in the contact zone under supergene phosphorites.

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GEOLOGICAL AND MINERALOGICAL ASPECTS OF APATITE MINERALIZATION,
SELIGDAR ORE DEPOSIT

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Several generations of apatite in the Seligdar ore deposit have been recognized, on the basis of morphologic and genetic indicators, during petrographic and geochemical studies. It has been established that typomorphic features may be a criterion for elucidating the origin of apatite.

Because of the need for assuring the agricultural economy of Siberia by means of mineral fertilizers, especially phosphate fertilizers, the problem of exploration for raw materials in this region is obvious. Of special interest is the apatite content of the Aldan Shield, including the huge Seligdar apatite ore deposit (with reserves estimated at 85 million tons of P_2O_5). The geology of this deposit has been studied by numerous authors [1-4]. The ore is restricted to the Nimgerkano-Timpton block and occurs at the intersection of the Tomotsk and Yukhtinsk fault zones; it is localized in the folded Archaean basement, which contains metamorphic rocks of the Upper Aldan and Fedorov suites of the Iengr series.

The deposit is roughly rectangular in shape, with the long dimension oriented north-west-southeast. The northwestern border is exposed in outcrop, while the southern part is concealed by a thin cover of Vendian to Lower Cambrian terrigenous and carbonate rocks intruded by Mesozoic syenite porphyry sills.

In cross section the deposit is an asymmetrical cone with a steep northeast side and gentle southwest side. Ore mineralization has been traced down to 1600 m without encountering pinchout or depletion of the P_2O_5 content.

Unconformable breaks, fault zones, and joint systems filled with serpentine-chlorite and quartz-chlorite-sericite metasomatites occur widely within the ore body. Syenite porphyry and shonkinite dikes are found both within the ore body and outside of it.

Apatite-bearing fine- to medium-grained calcite-dolomite rocks with thin interbeds and lenses of quartz-carbonate sandstones, siltstones, and pelitic limestones and dolomites make up part of the deposit. At depths greater than 300 m, lenses and interbeds of sulfate-carbonate rocks are found. The actual apatite mineralization is localized in essentially dolomitic marble. The average P_2O_5 content is 6.2%. The country rocks are schists and gneisses in which the P_2O_5 content is 0.21% [2].

The main rock-forming minerals in the apatite-bearing rocks are dolomite, calcite, quartz, martite-hematite, apatite, and phlogopite. Present in lesser amounts are hydrogoethite, gypsum, serpentine, talc, and pyrrhotite. Sphene, zircon, and garnet occur as accessory minerals.

The qualitative chemical composition of the ore is quite stable. The quantitative characteristics (mineralogical and especially textural) are not constant, however, and vary with both depth and location in the deposit.

Overall, two basic ore types are recognized: calcitic and dolomitic. These are further subdivided into a number of varieties depending on the predominant mineral impurity (mainly quartz and martite). Varieties that are mainly apatitic (quartz-apatite, martite-apatite) are rarely encountered. The average chemical and mineralogical composition of the ore, calculated from a large number of average samples, is presented in Table 1. The characteristic textures in the ore deposit are massive or banded, with zones composed of apatite and martite alternating with ore-free carbonate.

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TABLE 1. Average Chemical and Mineralogical Composition of Ore in the Seligdar Deposit

Component	Content, wt. %	Component	Content, wt. %
P ₂ O ₅	6,2	ELn ₂ O ₃	0,2
CaO	10,7	Apatite	14,6
MgO	14,1	Dolomite	59,4
CO ₂	30,1	Calcite	4,5
SiO ₂	13,4	Quartz	13,0
Fe ₂ O ₃	3,5	Martite	3,2
SrO	0,01		

Some areas, where the ore has been leached out, are cavernous. The cavities are filled with quartz, gypsum, hematite, and secondary dolomite. The overall texture of the rock is porphyroblastic. The groundmass is fine- to medium-grained, and essentially carbonate in composition. Irregularly distributed apatite, commonly in streaks and bands, is predominant in the porphyroblasts. The amount of apatite ranges from 0.3 to 75% and averages about 15%. The apatite porphyroblasts usually take the form of regular prismatic crystals 1 to 5 cm in length with well developed prism (110) and bipyramid (0111) faces. Three main varieties can be recognized on the basis of morphologic and genetic indicators.

1. Coarse (1.5-50 mm) dipyramidal-prismatic crystals, colored waxy-brown by finely dispersed inclusions of hematite and in places martite, with which a direct correlation is observed. Good prismatic cleavage and strong jointing are noted. A typomorphic feature of apatite of this type is its sharply expressed metacrystalline aspect, characterized by its "jacket" habit (Fig. 1), with a not very distinct crystalline outline, as if partially melted, and the ubiquitous presence within the apatite crystal of nonreplaced material; such grains within the metacrystal are commonly oriented the same as the enclosing material. Apatite of this type makes up 65-70% of the total. Indices of refraction are $n_o = 1.637 \pm 0.002$, $n_e = 1.633 \pm 0.002$, $\alpha_o = 9.385 \pm 0.002 \text{ \AA}$, $c_o = 6.833 \pm 0.002 \text{ \AA}$.*

2. Finer (0.1-1.5 mm on long axis) dipyramidal-prismatic crystals, light gray to light waxy in color, with irregular distribution of finely concentrated ore minerals. It makes up 20-25% of the total. Indices of refraction are $n_o = 1.639 \pm 0.002$, $n_e = 1.633 \pm 0.002$, $\alpha_o = 9.385 \pm 0.002 \text{ \AA}$, $c_o = 6.869 \pm 0.002 \text{ \AA}$.

3. Apatite of the third type occurs as fine and medium crystalline (0.1-1.0 mm) grains and aggregates of irregular to rounded shape, either greenish gray or colorless. Indices of refraction are $n_o = 1.630-1.635$, $n_e = 1.625-1.635$, $\alpha_o = 9.387 \pm 0.002 \text{ \AA}$, $c_o = 6.870 \pm 0.002 \text{ \AA}$. It occurs in markedly subordinate amounts and makes up no more than 5% of the total amount of apatite. A typomorphic feature of this variety is the absence of jointing and microinclusions of more minerals. This, as well as its restriction to areas of crushing, attest to the formation of this type of apatite in a later stage and to an association with processes of recrystallization.

In the upper part of the section, in a Proterozoic weathering horizon, phosphate minerals are found which are similar in characteristics to francolite and which may be considered a type IV (fourth generation) apatite in the deposit. Indices of refraction are about 1.615-1.620.

The chemical composition of the Seligdar apatite (Table 2) are an important typomorphic feature. It is interesting to note that the different types of apatite are quite similar in chemical composition (as they are in optical properties and unit cell parameters). They are characterized by some quantity of SiO₂, CO₂, and Fe₂O₃, associated with micromechanical admixtures of quartz, clay minerals, carbonates, and martite, and lesser amounts of fluorine.

The average F content in the mineral is 2.52%, and the ratio F/P₂O₅ is 0.065 (for comparison, the average F content in the Khibiny fluorapatite is 3.2%, and F/P₂O₅ is 0.08).

The fluorine deficit in the apatite, and also the higher indices of refraction and the parameter α_o , compared to fluorapatite (see Table 2) suggests that the phosphate mineral in the Seligdar deposit is fluorohydroxylapatite. Its formula, calculated on the basis of

*X-ray determinations provided by N. P. Bel'skaya.

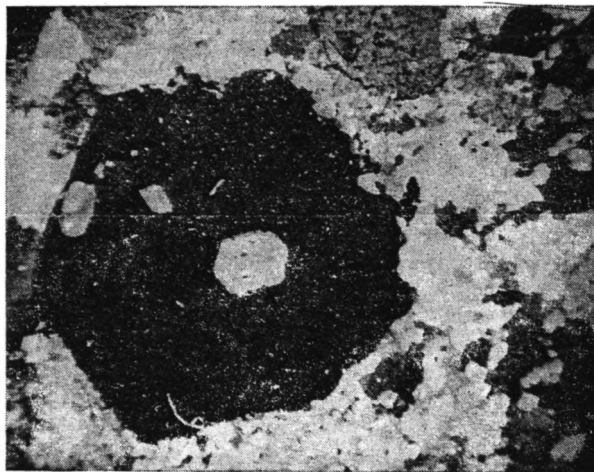


Fig. 1. Inclusion of dolomite (light colored) in the center of an apatite metacrystal; crossed nichols, $\times 220$.



Fig. 2. Inclusions of monazite (MO) in apatite (A), plane light, $\times 430$.

chemical analyses, can be expressed as $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_{1.4}(\text{OH})_{0.6}$. Moreover, it is characterized by always having a certain amount of sulfate ($\text{SO}_3 = 0.3\text{--}0.8\%$) and a small content of Sr, the average amount of which never exceeds 0.1%.

Certainly, the most significant geochemical feature of this apatite is its enrichment in rare-earth elements. I. S. Smirnova, using x-ray spectral methods on a "fluoroprint" device, has determined the total REE content in the apatite to be about 1%. The REE composition and distribution in apatite at Seligdar and Khibiny have been determined by V. V. Ermilov on the instrument "Mikroskan-5" (Table 3). The REE spectrum is selectively cerian. The apatites are quite similar in REE content, but differ sharply in strontium content.

The question of the type of rare-earth mineralization present in the Seligdar ore has long been debated in the literature [5-7]. Calcium phosphates are generally characterized by extensive isomorphism and no doubt, the possible entry of Sr and REE into the apatite structure. However, detailed mineralogical studies have shown the presence of two types of rare-earth mineralization [8]. About 60% of the total rare earth elements, and apparently all of the Sr, enter into the apatite structure, isomorphously replacing Ca (by analogy with the Khibiny apatite) [9]. The remainder are included in other minerals, such as monazite, $(\text{Ce}, \text{La}, \text{I}, \text{Th})\text{PO}_4$, and possibly others that are very difficult to recognize because of the extremely small size of rare-earth minerals [7]. Monazite occurs as inclusions in apatite grains, and under the microscope appears as colorless, roughly oval grains 20-30 μm in size with distinct birefringence and interference colors up to second order blue-green (Fig. 2). It may tend more towards first generation apatite. Monazite is clearly recognized by x-ray in insoluble residues after treatment of powder with 3% HCl for removal of phosphate and carbonate particles.

TABLE 2. Chemical Composition and Some Physicochemical Features of Apatite in the Seligdar Deposit

Component	Type I apatite	Type II apatite	Apatite from monofractions	Apatite from averaged samples	Apatite fraction from concentrate	Khibiny apatite
P ₂ O ₅	39,20	39,57	39,38	39,27	39,60	39,40
CaO	52,29	52,93	52,53	51,93	50,70	50,20
F	2,71	2,63	2,73	2,54	2,50	3,20
Fe ₂ O ₃	0,95	0,82	0,96	1,01	0,50	0,40
Al ₂ O ₃	0,54	0,70	0,27	0,12	0,70	1,90
MgO	0,26	0,31	0,39	0,23	0,80	0,50
MnO	0,02	0,01	0,02	Not det'd.	Not det'd.	—
SrO	0,1	0,1	0,27	0,1	0,1	2,7
Na ₂ O	0,15	0,30	0,17	Not det'd.	Not det'd.	—
K ₂ O	0,02	0,01	0,02	Not det'd.	Not det'd.	—
TiO ₂	0,02	0,02	0,03	»	»	—
SiO ₂	2,01	1,86	1,92	1,92	2,7	—
ΣLn ₂ O ₃	0,9	1,0	0,66	1,0	1,1	1,1
CO ₂	0,94	0,61	0,63	1,20	1,50	—
SO ₂	0,26	0,35	0,24	Not det'd.	Not det'd.	—
Cl	0,15	0,02	0,17	»	»	—
—O=F,Cl	—1,20	—1,11	—1,23	—1,06	—1,05	—
Σ	99,32	99,51	100,1	98,26	99,15	—
F/P ₂ O ₅	0,069	0,066	0,063	0,064	0,063	0,081
n _D	1,637±0,002	1,637±0,002	—	1,636—1,638	—	1,634±0,002
n _g	1,633±0,002	1,633±0,002	—	1,632—1,635	—	1,629±0,002
a ₀ , Å	9,385±0,002	9,385±0,002	—	9,375±0,002	—	9,37

TABLE 3. Rare-Earth Element Content in Seligdar and Khibiny Apatites, wt. %

Deposit	Sr	Ba	La	Cl	Nd	Sm
Seligdar	0,11	0,02	0,22	0,63	0,32	0,08
Khibiny (Yukspor)	2,12	0,08	0,24	0,31	0,19	0,03

It is well known that the typomorphic features of apatite are important criteria for determining the origin of the deposit. Analysis of the physicochemical features of the Seligdar apatite cannot, however, provide an unequivocal answer to that question. The fluorine deficit is on the whole a characteristic of carbonate-type apatite [10] as well as of tectonically active, metamorphosed zones of sedimentary deposits [11]. Apatites from carbonates are characterized by increased SrO content (0.2-0.7%) however, and apatites of sedimentary-metamorphic origin, which are similar in nature to the Seligdar apatite, are characterized by a low content of rare-earth elements. A number of factors indicate a metasomatic nature of the apatite mineralization, the chief ones being the typomorphic aspect of apatite crystals of the first two generations and especially the nature of the mechanical inclusions in apatite of generation I, which were trapped during growth of the crystals and are mainly carbonate and quartz.

The restriction of the deposit to a fault zone, and the presence of phosphorous in the country rock (according to Parfenov and Yudin [2]), suggest that apatite mineralization was primarily associated with mobilization of disseminated phosphorous in the country rock during granitization. During this process carbonate rocks served as a unique lithologic trap.

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SODA LAKES OF MONGOLIA

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In the article, we classify the geochemical types of lakes in Mongolia using cluster analysis and demonstrate the widespread occurrence of soda-type lakes and show the distribution of such lakes over the Mongolian territory. Features associated with the mineralization of the lakes are also noted.

Soda mineralization is widespread in lake waters. According to the data of various authors, soda waters constitute more than a third of the total volume of lake waters [2, 4, 18]. However, the major portion of such soda waters are characterized by low salt concentrations and are often classified as fresh-water. Lake waters of a soda character are especially widespread in Mongolia and the Transbaikal. Approximately half of the mineralized lake waters of this region apparently fall within this category and are located in Mongolia. The majority of large lacustrine basins here (Ubs, Khirgis, Khar-Us, Bon-Tsagan, Dergen, Telmen, Shar-Buridin, Zun-Nur, Barun-Torei, Oigon, Sumiin, and others) have soda components in their salt compositions. The waters of one of the large fresh-water lakes of Mongolia, Khubsugul, also belongs to the soda-type (as do the waters of Lake Baikal). Many investigators have pointed to the occurrence of soda mixtures among the lake waters of Mongolia [3, 8, 13, 19], noting, however, the extremely limited information available on the geochemical composition of the mineralized lakes of Mongolia and noting the need for studies of the salt compositions and resources of the lakes, including studies from the point of view of the soda components involved.

Features associated with the geological structure, climate, regime, composition of the ground waters, and soils in the different areas of Mongolia helped to form saline lakes with various salt compositions and mineralizations [4, 6, 7, 24], leading to the formation of salt beds of differing compositions in extreme cases (halite: Lake Tsav-Dam, Sangiin-Dalai, Davsan, Defter, and Gurvan-Tés; soda: Bult, Tsaidamyn, Shar-Nur, Borogtsaigiin, and Toson; mirabilite: Kharyin and a whole series of other beds with mixed compositions of salts and more fines).

While processing information on the saline compositions of the lake waters, the need arose to delineate detailed hydrochemical types with the use of large amounts of statistical data. This eventually made it possible to investigate similar research targets and to generalize data concerning prospective uses of the saline-lake resources. However, repeated attempts to associate certain hydrochemical types of saline lakes with one or another set of conditions involved in their formation often led to ambiguous results. In the first place,

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this was due to the fact that, on the basis for the water-composition systematizations of the saline lakes [1, 9, 12] in use, criteria were posited which did not taking into account all of the information concerning the samples being classified (the number of parameters in the classification) (often a small number), and the internal relationships between the hydrochemical components. In addition, the very methodology of evaluating the significance of geological or climatological connections between different types of saline lakes was based upon the use of averaged values that, to a significant degree, obscured the real picture of their hydrochemical diversity.

Delineations of stable "hydrochemical types" of mineralized waters on the basis of a visual analysis of various diagrams constructed in the coordinates of the cation-anion composition of the water are usually distinguished by a significant ambiguity [13]. This is connected with both the incompleteness of the information used to construct the diagrams and the subjectivity of the investigator when drawing boundaries between geochemical types. Although there are many different ways to construct classificational diagrams at present; in the majority of cases, they can be reduced to selections of different (including composite) hydrochemical indices [1, 7, 17, 22, 23, 26].

As an example, we will discuss the use of one of the well known diagrams, $\text{Na}^+ + \text{K}^+$, $\text{Ca}^{2+} + \text{Mg}^{2+} - \text{Cl}_1^- + \text{SO}_4^{2-}$, $\text{HCO}_3^- + \text{CO}_3^{2-}$ applied to the targets of our study [17]. In the diagram (Fig. 1), data are presented on the compositions of the waters in the saline lakes of Mongolia. It is evident that an attempt to delineate "hydrochemical groups" in this case leads to an identification of only two "hydrochemical types": Type I, which are essentially hydrocarbonate waters; and Type II (a multitude of markedly spread-out points), which are predominately sodium chlorides. No more detailed classification of the collection of points into "groups" is possible within the framework of the hydrochemical indices used in this case.

On the basis of the two "groups" delineated, one might logically switch to a more suitable division into subgroups within other coordinates, in particular, coordinates of anionic composition only (since the greatest spread of points in the diagram under consideration is precisely that occurring along the HCO_3^- , CO_3^{2-} , Cl^- , SO_4^{2-} axis).

However, repeated divisions into groups generally do not aid in coming to a more precise characterization of the structure associated with the collection of data under study, since the actual shapes of the distribution functions for the frequencies of occurrence (all of the classificational diagrams were constructed during analyses of such functions) are multidimensional, with features which cannot be reduced to the two- and three-dimensional cases.

The use of more complex "hydrochemical indices" as coordinates (a sum of cations and anions, their ratios, etc.), leads to a disappearance or loss of some of the original information in the majority of cases; this is connected with using nonlinear transformations (ratios) in some cases and with ignoring the scatter of individual components in others (the use of a sum).

While far from belittling the value of the various "hydrochemical indices" and diagrams classifying mineralized waters and resulting in a fairly tight-knit view of classification [1, 7, 11, 17], attention is beginning to be directed toward the fact that the "geochemical" information available at the present time is huge in volume (hundreds and thousands of analysis on tens of components) and difficult to process by traditional methods.

The need to process "hydrochemical" information in such great volumes inevitably leads to solving problems of "hydrochemical classifications" with the aid of a computer.

In order to process the data we obtained on the composition of the saline lakes of Mongolia (approximately 200 objects of study), we used one of the cluster-analysis methodologies which allowed us to classify data of any dimensionality (a 7-component dimensionality, in our case) in samples with any form of distribution function for the frequency with which concentrations of elements were encountered [10, 15]. The processing was carried out on a CM-4 computer at the Laboratory of Mathematical Geology at the Geological Institute of the Academy of Sciences of the USSR.

The cluster analysis allowed us to find the following numbers of groups at each step of the alomeration within the framework of a given sample (233 analyses): 1st step) 94; 2nd step) 26; 3rd step) 36; 4th step) 18; 5th step) 15; 6th step) 8; 7th step) 5; 8th step) 4; 9th step) 3; 10th step) 1.

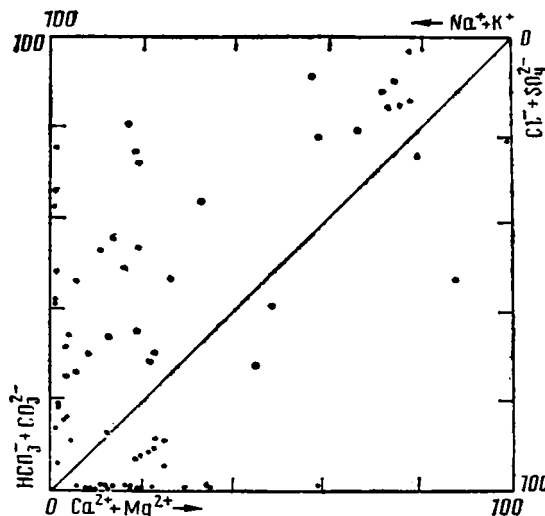


Fig. 1. Classification diagram for the salt compositions of the lake waters of Mongolia.

We chose the 5th step of the alomeration (15 clusters) as our working model, since the preceding steps of grouping primarily reflect local variations in water composition, while the subsequent (6th step) yields too deep a division of the sample into sulfate-chloride, chloride-sulfate, carbonate-chloride, and chloride, with the remaining four clusters represented by individual points.

Out of the 15 hydrochemical types of salt-water basins delineated, eight, accounting for 95% of the sample, are the most representative; the remaining seven types contain only one or two points and are not discussed further.

The compositions of the eight delineated clusters of saline lakes are presented in Table I along with the mineralizations and numbers of points included in the clusters. Fluctuations in the salt composition of the lake waters can be functions of not only of the compositional differentiation within the object of study but also of meteorological and seasonal climatic factors. Despite this, data of several analyses from a single research target taken at different times and at different places, fall within the same cluster; this indicates a stable hydrochemical "framework" of actual research targets and the possibility of classifying such research targets by this method.

One of the characteristic features of hydrochemical specialization within the groups delineated is a fairly stable correlational relationship between the degree of mineralization and the types of cationic-anionic compositions of the lake waters. The most mineralized lakes, with the exception of several lakes of the 6th cluster, belong to the soda type (clusters 2, 4, 6, and 7); lakes with maximum mineralization belong to the chloride type (clusters 3 and 5); lakes with intermediate or mixed composition and lakes of the sulfate type have average mineralizations (clusters 1 and 8).

In addition to investigating the distribution of components within each group (the hydrochemical parameters of the cluster), we studied the distribution of the groups within the territory of Mongolia, and also the connection between distribution and the geological situations and features of mineralization. As a result, the following brief characterization of the clusters was obtained.

1st Cluster. Lakes of this type (maximum sulfate salts) predominate in northern Mongolia, somewhat south of Lake Khubsugul. This is a mountainous region where deep lacustrine basins frequently coincide with the massifs of ancient metamorphic rocks. The mineralization of the water here is 25-40 g/liter. A second small subregion of this cluster is located slightly south of Mt. Ulan-Bator in a hilly territory distinguished by a drier climate. The mineralization of the water here is 50-70 g/liter.

The **2nd cluster** is represented by soda lakes (components of a trona-type composition predominate). Large amounts of Ca- and Mg-carbonates are present in the composition of the salts, along with Na. Lakes of this type are situated in the central and (to a lesser extent) eastern

TABLE 1. Average Values of the Cationic-Anionic Composition of Salts and Mineralizations in Types (clusters) of Saline Lakes in Mongolia, % of Total Ions

Cluster	Mineralization, g/liter	Na ⁺ + K ⁺	Mg ²⁺	Ca ²⁺	Cl ⁻	SO ₄ ²⁻	CO ₃ ²⁻	HCO ₃ ⁻	No. of points
1	25-40 50-70	20,05	2,43	0,0	13,89	47,76	0,87	2,51	20
2	0,5-1,5 2-4	9,68	6,43	7,04	7,41	8,86	0,87	56,67	15
3	50-180	22,01	8,86	0,70	47,21	17,23	0,0	0,0	18
4	2-6	30,37	1,74	0,0	4,17	6,89	13,86	40,12	6
5	200-300 20-10	33,45	1,74	0,0	49,53	9,35	0,87	1,5	43
6	2-8 150-300	31,69	2,78	0,7	24,07	8,37	14,30	14,04	35
7	2-5	26,41	3,82	0,71	11,57	27,08	4,77	21,06	36
8	10-30 50-120	28,17	3,83	0,0	29,62	29,54	1,30	3,51	52

areas of Mongolia. The mineralization of the water is low: 2-4 g/liter. A second subregion can be delineated in western Mongolia within the salmon region of Khovd. A still weaker (0.5-15 g/liter) mineralization of the water is found here. Asoda component can form here due to salts leached from soils of various types [5, 16, 20].

The 3rd Cluster are chloride-sulfate lakes of the mountain or near-mountain regions of Mongolia and Bobissk Altai distinguished by high concentrations of Mg cations in the salt composition, apparently due to the presence of rocks of an alkaline composition (Tonkhil, Ikhes, Biger, and others). The mineralization is average, sometimes high (50-180 g/liter).

The 4th Cluster are weakly mineralized soda lakes (2-6 g/liter) predominantly situated along the middle course of the Kerulen River. These are frequently pinched off portions of old stream channels.

The 5th Cluster is one of the most numerous of the groups of lakes. Halite predominates in the salt composition. The mineralization of the water in the east and northeast of Mongolia reaches 100 g/liter in such lakes. The majority of lacustrine deposits of NaCl in the Mongolian territory (Tsokhor, Sangiin-Dalai, Gurvan-Tes, and others) belong to this cluster.

The 6th Cluster are soda lakes with carbonate and bicarbonate salt compositions and also admixtures of chloride and sulfate compositions. They occur predominately at the northeastern border, where there are many lakes of this type with weak (2-8 g/liter) mineralizations. However individual lakes with high (150 g/liter) mineralizations do occur: Tsaidamyn; central Mongolia), Bult (northwestern Mongolia), Shar-Nur, Toson (eastern Mongolia) and others.

The 7th Cluster are small soda lakes occurring between the Khangai and the Khentei mountain masses, the Basin of the Great Lakes, and also in the east of Mongolia. They are distinguished from the other types of soda lakes by high quantities of sulfate salts. The mineralization is weak (2-5 g/liter).

The 8th Cluster, chloride-sulfate lakes, are represented by two subgroups: the first to the north and south of Mt. Ulan-Bator, a region of average-sized lakes and mineralizations of 10-30 g/liter (a semidesert zone with a higher mineralization of 50-120 g/yr is situated to the south); the second is in western Mongolia, where large lakes predominate. The mineralization here is 5-20 g/liter.

From the information presented, it is evident that the majority of objects of study in the 5th Cluster are of interest for research studies on NaCl (including studies from the point of view of salt reserves). In the 6th cluster, the objects of interest are highly mineralized soda lakes, sometimes with reserves of soda minerals. The lakes of the western mountain regions (Cluster 3) may be of regional significance. A series of large lakes of the 8th Cluster apparently possess large potential reserves; therefore an investigation of the directions from which material is supplied to them, along with a study of the geological structure taking into account the composition of the ground waters and the hydrogeological features of the region [13, 19], may lead to the discovery of new sources of highly concentrated mineral

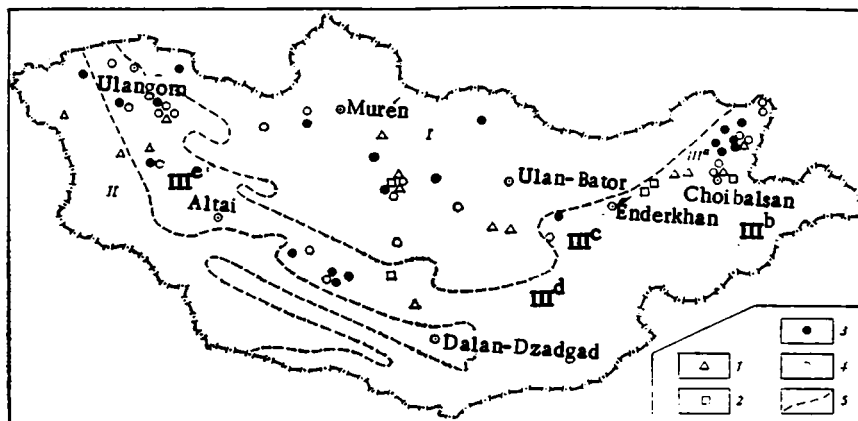


Fig. 2. Distribution pattern of saline lakes in the territory of Mongolia. 1-4) lakes of the 2nd, 4th, 6th, and 7th Clusters, respectively; 5) borders of hydrogeological regions (I: Khangai-Khentei, II: Mongolia-Altai and Gobi-Tien-Shan), III: artesian waters of intermontaine basins and ground waters of positive interbasin structures. Subregions: IIIa) Choibalsan; IIIb) Tamsagskii; IIIc) Nilginskii; IIId) Gobi; IIIe) Basin of the Great Lakes.

salts. The remaining types are probably less promising as salt reserves; however, they are of undoubted interest from a genetic point of view.

As is evident from the data presented in Table 1, four of the eight clusters have a soda compositional characterization (clusters 2, 4, 6, 7); the majority of the objects of study show comparatively weak mineralization. The distribution of the soda lakes in the various clusters over the territory of Mongolia is shown in Fig. 2. The overwhelming majority of these are concentrated in the northwest and also in the Basin of the Great Lakes and in the southern part of Doliny Lake. The exceptions are in the south and the extreme western and eastern regions of Mongolia.

Deserts predominate to the South. Lakes of a chloride composition, sometimes with significant salt reserves (Lake Gurvan-Tés) are encountered, along with widely occurring solonchaks.

In the region of the Mongolian Altai to the south, where abundant Paleozoic rock complexes represented by meta-effusives, and quartzites, jaspers are present along with granites, granodiorites, and crystalline schists but where the ground waters of the corresponding hydrogeological region are distinguished by high sulfate content [14], mineralized lakes are comparatively few. Sulfates and chlorides of sodium with high magnesium contents (the majority of points in Cluster 3) predominate in the composition of the lake waters.

In arid-step and semi-desert zones in the extreme east, highly mineralized lakes of a chloride profile occur (composition of ground waters-sodium chloride-Subregion IIb).

The degree of influence of ground waters on the composition of the soda lake waters can be evaluated by taking into account the geological structure of the regions and the hydrogeological regionality.

A large number of soda lakes (Cluster 6) coincide with the Choibalsan hydrogeological subregion (see Fig. 2). Lower Cretaceous deposits are ubiquitous here; they are represented by the rocks of the Sharilinsk, Tsagantsabsk, and Deunbainsk suites. Effusive rocks corresponding to andesite-basalts, basalt-effusives, and porphyrites predominate. The primary aquifer complex (Lower Cretaceous) is distinguished by slight porosity and a fairly high (up to 4 g/liter) chloride-hydrocarbonate mineralization, whereas the waters of the Tertiary deposits are very weakly mineralized and have a chloride-sulfate-hydrocarbonate composition. Low-amplitude neotectonic movements (Quaternary and Recent) resulted in the development of a series of faults and a zone of distinct jointing (extended linearly to the north-east along the borders of large depression zones). Mineral carbonates and weakly mineralized waters containing Mg, sometimes with Na as well, coincide with the faults and the jointing.

The peculiarities of the geological structure and composition of the ground water of this subregion of Mongolia indicate that the faults and joints play a definite role in creating the waters in the soda lakes of Cluster 6 and, particularly, Cluster 7. This province of mineral waters is a continuation of an analogous province of mineral waters in the USSR widely present in the Transbaikal [2, 19].

Lakes of the soda type are fairly widely distributed in the territory of the Basin of the Great Lakes. The geology of this region is insufficiently studied at present, both because of the complex structure and in connection with the limited quantity of borehole data available. The pre-Paleozoic and Paleozoic complexes of rock along the edges of the basin were broken through by intrusives of various ages and were strongly dislocated. The rocks that lie on the basement are continental deposits of Jurassic, Cretaceous, and Neogene-Quaternary age represented by sandstones, gravelites, limestones, clays, coals, lacustrine muds, and sands. To the east, they are aeolian. The data on the ground water here are somewhat varied in origin and fragmentary. It is thus a complicated task to precisely estimate the degree of influence of various factors (climate, soils, rock compositions, and ground water, etc.) upon the formation of the soda components. However, this region is one of the most interesting in the territory of Mongolia from the standpoint of studying the formation of salts.

Soils, and, in particular, the chestnut soils widely distributed over the Mongolian territory and distinguished by weakly alkaline reactions, minimum chlorides, and elevated amounts of sodium carbonates, play a definite role in forming the soda components of the lake waters. In addition, the concentrations of carbon dioxide and oxygen increase during the decomposition of organic material in the soils and during other biochemical processes [6, 18]; these events jointly facilitate the creation of a carbonate environment. This apparently explains the fact that the presence of such soils toward the northern border, where their elution by meteoric waters takes place more actively, coincides with a large number of soda lakes (Cluster 2 and 7). The degree of salinity of the soils in this case undoubtedly reflects the mineralization of lacustrine waters with no place to drain. The mineralization reaches 18% in the Basin of the Great Lakes, for example, and 11% on the Eastern-Mongolian plain, 4% in Khangai and Khentei, and 2% in Mongolian Altai. In addition, a primary or secondary nature of the salts in the soils can be said to exist here, since evaporation of ground water located near the surface can facilitate salination.

Under the arid and semi-arid conditions of Mongolia favorable to evaporation, river waters of carbonate composition which feed into the settling and draining conditions of oxbow lakes formed from pinched, unstable old stream channels create soda lakes of a definite geochemical type in a number of cases (Cluster 4).

Soda lakes with high mineralization and, in a number of cases, with soda-bearing bottom deposits are of special interest, although comparatively few such lakes have been discovered within the territory of Mongolia. We will discuss several of these in more detail.

Lake Bult (Mongolian for "soda") is located within the salmon region of Tés in the northwestern area of Mongolia and coincides with the eastern portion of the Ubsnurk basin. A group of lakes are present here in an area with low relief extended somewhat from the west to the east (the Bultyn Khotgor Basin). The majority of these lakes are drying up; they are sometimes weakly mineralized and fresh to some extent. Lake Bult stands out among these because it has water of consistently high mineralization and also has salt deposits. It was well known to the population since ancient times and the soda removed was used for household needs. The first scientific data concerning the lake was obtained by I. E. Turishchev in 1942. Subsequent research efforts were carried out by many scholars: D. Davasyren (1961), Sh. Luvsandorzhem (1958 and 1966), and Zh. Sum'ei (1973). V. P. Petrov, A. A. Rasskazov, and B. Zhamba, coworkers of the Soviet-Mongolian expeditions, worked in the region of the lakes in 1980-1982. The drilling of a series of boreholes indicated that Neogene and Quaternary sands were present in the region. The barkans of the Borig-Del sands occur somewhat further to the south. The shape of the lake basin of Lake Bult differs sharply from the shapes of the other lakes in the region; it is an almost perfect circle (100 m in diameter) with fairly steep shores uncharacteristic of the local relief and reminiscent of a funnel-shaped structure. The rocks enclosing the lacustrine stratum are fluvial sand deposits up to 10-m thick. These are gradually replaced in the lower portion of the section by black, homogeneous, very plastic clay (up to 2 mm in thickness) with the smell of hydrogen sulfide (see Fig. 3). A buried, black, coarsely crystalline soda layer (up to 1.5 m in thickness) lies above, frequently with an admixture of clayey material. The Na_2CO_3 content varies from 14 to 54% (according to the data of Zh. Sum').

Further along the section, there is a black, plastic clay (up to 0.05 m) which takes on an ever more greenish tint upward along the section. This clay is overlapped by the soda of a novosadka (salts deposited during a single season); the thickness of the novosadka alternates in a periodic fashion from 0.1 to 0.4 m within a yearly cycle. The thickness of the brine reaches 1 m. The Na_2CO_3 in the dry sediment of the novosadkha amounts to 60-67% of the total; other components are 10-12% Na_2SO_4 , 3% NaCl , 0.5% MgCO_3 , CaCO_3 , 5-25% not determined. Mirabilite enters into the mineral composition of the novosadkha along with the soda. The chemical composition of the brine is presented in Table 2. The paucity of data on the composition of the ground water in the region do not allow us to come to any conclusion concerning the widespread occurrence of soda mineralization here. The majority of the neighboring lakes are distinguished by either a chloride or chloride-sulfate salt composition (Davsan, Davst, and others). Peculiarities concerning position within the relief, the morphology of the shores, and the specifics of the water compositions allow us to suggest the presence of an "independent" source of soda components. This is possibly connected with a local elution of sandy or carbonate rocks by ground water. A chalk bed found in this region by Zh. Sum' (without detailed characterization) may have been the cause.

Another research target with highly mineralized soda water is a chain of lakes situated in a valley of sublatitudinal strike. The last basin of erosion associated with the lakes is Lake Tsaidamyn Bara (1×1.5 km) located 25 km north of lake Ugi. All of the lakes are comparatively small (150×200 m) in size, with the exclusion of Lake Tsaidamyn Bara (1×1.5 km). The pH increases regularly from 8 to 10 in Lake Tsaidamyn Bara as one moves with the direction of flow along the valley. Although there are no deep-well salt beds here, the layer of novosadkha reaches 15 cm in favorable years; this is enough to allow soda to be extracted for domestic purposes. From a geological perspective, the region is infilled by rocks of Carboniferous and Triassic age and also by Quaternary deposits in the central portions of the valley (tracing out a large sublatitudinal fault) represented by sands, loams, and, more rarely, pebble beds. The northern border is composed of rocks of the Avzakhsk suite (T_2) represented by an alternation of medium-coarse grained conglomerates with sandy cement, interlayers of lava breccias of an andesitic-basaltic composition, and sandstones. Carbonates and also silts are present, along with hydromica, in the cement of the sandstones. Judging from the morphological features on the surface of the region, the primary flow of water is directed from this massif. Fine-grained sandstones of the Middle-Upper Carboniferous (Artel'sk suite) predominate on the southern side. The formation of the soda components in the region takes place as a result of the elution by the surface waters of the mountain mass (and flow from successive concentrations). The cation portion of the salts might be formed as a consequence of the decomposition of feldspars, sandstones, and plagioclases, since the anionic portion is due to carbonate material (not excluding the effect of near-fissure waters). Soda lakes with a similar mechanism of salt formation but with less mineralization are widespread within regions of the central and western portions of Mongolia.

All of the northeastern portion of the Mongolia territory is distinguished by a large number of mineralized lakes of the soda or chloride type. This region is a southern extension of the occurrence of soda lakes in the Transbaikal area [2]. The majority of modern soda lakes in this part of Mongolia are of comparatively low mineralization and are frequently relicts of larger, ancient continental water basins [21]. These include Barun-Khaimor, Khult, Khukh, Tsaidam, Ikhé-Dzosu, Tosogiin, and the series of lakes of the Sumiinursk depression tracing out a large fault zone of northeastern strike formed by neotectonic movements. The soda components of these lakes was due to the development of both surface and ground water of soda specialization on the one hand, and, on the one hand, to the structure and composition of the rocks of the basement, and to the sedimentary complexes of the depression zones. Lake Sumiin, where the formation of soda-lake components is associated with the elution of a mass of sandy rocks by meteoric waters entering from southeastern granite and northern basaltic massifs can serve as an example (Fig. 4). The composition of the ground water of this hydrogeological province has a carbonate characterization; this, in conjunction with the drainless basin of the central portion of the Sumiinursk depression, results in the formation of mineralized waters of a soda composition under appropriate climatic conditions (the temperature of the air reaches 35°C). However, the question of the primary source of the carbon dioxide, which might be either of endogenous origin or connected with the surface climatic and biological factors, remains open.

Let us consider one of the few highly mineralized soda lakes in the southeast of Mongolia, Lake Toson (see Table 2), located near the Kerulensk State Economy Building, as an example.

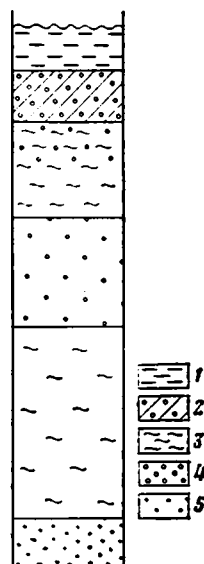


Fig. 3

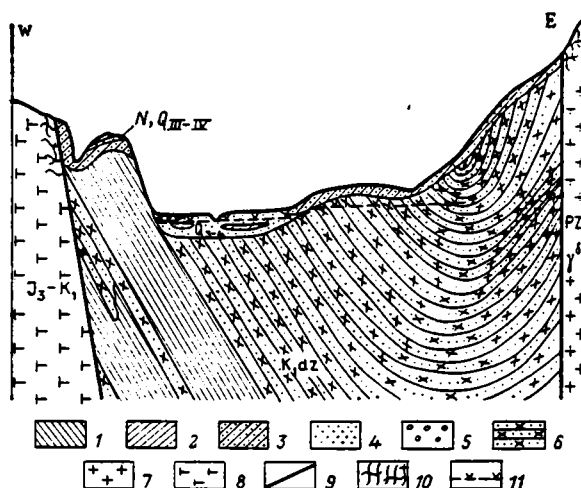


Fig. 4

Fig. 3. Schematic section of deposits at Lake Bult: 1) brine; 2) novosadkha; 3) clay; 4) buried soda-water pool; 5) sands.

Fig. 4. Schematic section of the Sumiinursk depression: 1) clay; 2) loams; 3) sandy loam; 4) sands; 5) boulders; 6) sandstones; 7) gneiss-type biotite granites and granodiorites; 8) andesite-basalts, andesites, and tuffites; 9) faults; 10) zones of jointing; 11) level of ground waters.

The position within the relief, the morphology of the shores, and the coincidence with a large fracture zone, along with a number of other factors, allow us to assume that factors of an endogeneous character may play a role here in forming the saline composition of the waters. Waters of the low-temperature mineral sources present in the northeastern portion of Mongolia (arshans) and associated with feeder regions to lakes (Khonkoryn, Arshanbulak, and others) may play a role in the formation of the salts in the salt provinces studied [14, 19]. In addition, the study of the temperature regimes of the region together with the mineral composition of the thermal waters aids in evaluating of the importance of the endogenous effect upon the salt compositions of waters both below and above the ground. A region of interest in this regard is the Minzhur country (coinciding with the same fault zone as Lake Toson, but located somewhat further north along this zone), where vents of hot gases ($T = 60^{\circ}\text{C}$ at a depth of 40-50 cm) along the contour of the area (diameter of 300 m) with clearly expressed (another size and color of vegetation) funnel-shaped cave-ins of soil. Rocks of dacitic and liparitic composition are abundant here; basalts, scoriaceous basalts, and tuffogenic formations of red and rose color can also be found. There are either white clouds or crusts (travertine-type) up to 2 cm thick at the locations of the gas vents. The regional phenomenon has been explained by several investigators [13] as due to the presence of subterranean coal fires. This explanation is apparently based upon the presence of burned slaggy and baked rocks (although how they have turned upon on the surface in this case is not understood), cave-in of soil, and the coal content of the depression zone. A previously obtained composition of the gas:

H_2S	CO_2	CH_4	H_2	N_2	Ar	He	O_2	Σ
Not det.	3,31	0,01	0,001	80,60	1,08	0,001	15,0	99,99
	11,65	0,001	0,001	86,86	1,48	0,001	--	99,98

does not allow for a definitive conclusion on this point. Moreover, the entire region of the Minzhur District, and also the neighboring hills receding to the northeast, are composed of analogous rocks with compositions and structure indicating active magmatic activity. The composition of the gas (in particular, the Ar content), the coincidence of other arshans with this fracture zone, and features associated with neotectonic movements allow us to assume a high permeability for this region.

The strong alkalinity of the environment of a soda lake with concentrated brine and high pH values facilitates an active transformation of silicate material brought into the lake and

TABLE 2. Composition of the Salts in Several Highly Mineralized Soda Lakes of Mongolia

Lake	Na ⁺ , K ⁺	Mg ²⁺	Ca ²⁺	Cl ⁻	SO ₄ ²⁻	CO ₃ ²⁻	HCO ₃ ⁻
Bult	102,0	0,1	—	10,8	65,4	77,2	7,3
	38,8	0,04	—	4,1	24,9	29,4	2,8
Taidamyn	27,1	0,02	0,002	19,2	6,9	13,1	3,3
	38,92	0,03	—	27,6	9,9	18,8	4,7
Toson	123,5	0,36	0,02	34,84	40,94	94,80	23,18
	38,9	0,11	—	10,97	12,89	29,85	7,30

Explanation. Values in g/liter are presented in the numerator; in the denominator: in % of total ions.

an intensive authigenesis of non-saline minerals [3, 25, 27]. The majority of the clays of highly mineralized soda lakes are very finely dispersed, frequently black (due to reworked organics) or green in color, sometimes with the odor of hydrogen sulfide. The clays of Lake Bult, for example, together with the terrigenous material and chemogenic carbonates, contain authigenic silicates: hydromica, chlorite, and a large quantity of smectite (Fig. 5), which can be identified on diffractograms (Sample 100) by the high intensity of the basal reflection (001) with $d = 14.7 \text{ \AA}$ (untreated), $18.9 \text{ \AA}$ (saturated with glycerin), and $10.1 \text{ \AA}$ (heated at 550°C). At appreciable depths along the section, a reflection with $d = 12.4 \text{ \AA}$ appears on the diffractograms of the samples (see Fig. 5, Sample 102); this appearance can be explained by the presence of a zeolite (an erionite type). The X-ray data from the clay samples of Lake Tsaidamyn Bara indicate a similar set of mineral clays.

A detailed study of the processes of silicate authigenesis in different hydrochemical circumstances (including soda environments) is of interest for understanding the "mechanisms" of transformation and redistribution of silicate material in harsh evaporative environments. Highly mineralized lakes of various hydrochemical types are unique "proving grounds" for studying such mechanisms.

In the long term, the processes of authigenic mineral formation in waters with not only soda but also chloride and sulfate profiles will be investigated in complete detail, in combination with the geological situation of the region.

For a further general systematization of the salt composition of the waters on the basis of multidimensional hydrochemical data, the cardinal problem of carrying out a comparative analysis of the compositions of the waters in different regions should be given consideration. The possibilities for computer processing of massive quantities of geochemical data now allow more detail in broader ranging factual material drawing upon information on minor elements, rare elements, etc. It is now possible to address the problem of systematically identifying stable hydrochemical types of salt-producing (including soda-bearing) basins. This, in turn, will make it possible not only to recognize the basic genetic patterns associated with the geochemical aspects of the salt compositions of the waters, but will allow a more effective evaluation of the promise of various territories for exploratory work.

We may draw the following conclusions.

1. The fundamental hydrochemical types of saline lakes in Mongolia have been identified on the basis of appreciable statistical data on their compositions.

2. We have shown the widespread occurrence of lakes with soda mineralization, the predominance of such lakes (in a typical ratio) over other types of hydrochemical lakes, and their distribution over the Mongolian territory.

3. We have established a statistical relationship between the degree of mineralization of a lake and its hydrochemical type (see Table 1).

4. The definitive factors associated with the hydrochemical aspect of the fundamental types of soda lakes are: the geological structure of the region, the regime, composition of ground water and peculiarities of neotectonic movements (Cluster 6); the compositions of the rocks of the distributive provinces, together with the arid and semiarid character of the climate (Cluster 2); the composition of the surface waters and the hydrogeological environment

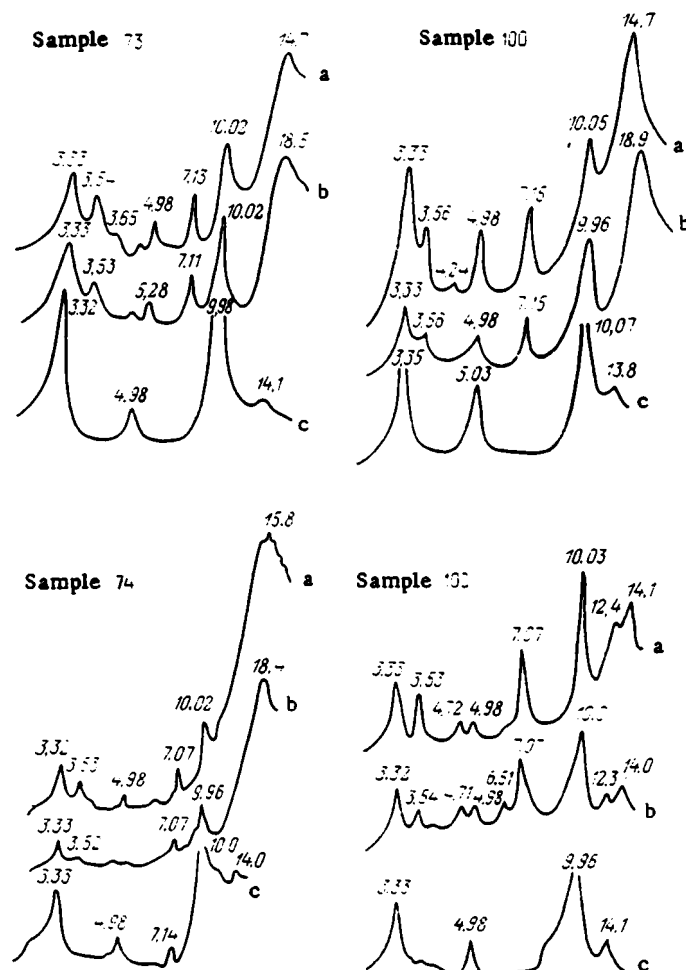


Fig. 5. X-ray diffraction patterns of clay samples from saline lakes. Samples: a) bottom; b) saturated with glycerin; c) heated at 550°C (samples 100 and 102 are from Lake Bult; samples 73 and 74 are from Lake Tsaidamyn Bara).

(Cluster 4). The lakes of Cluster 7, occupying an intermediate position with respect to composition between research targets with soda and sulfate characterizations, apparently have a polygenetic character.

5. The various factors enumerated above apparently play a role in the formation of highly mineralized soda lakes. In particular, an endogenous seepage of components facilitating soda mineralization of the waters may take place. The specific composition of the gases in bordering tectonic areas are an indication of this point as well as the other.

6. Features associated with the chemical composition of the waters of highly mineralized soda lakes determine the specifics of the silicate mineralization within the lakes, leading, in particular, to the formation of authigenic silicates, preferentially smectites and, in subordinate quantities, hydromicas, chlorite, and also zeolites.

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CONDITIONS OF CARBONACEOUS ROCK ACCUMULATION IN THE OSKOL'SK
SERIES OF THE LOWER PROTEROZOIC IN THE KURSK MAGNETIC ANOMALY
(KMA) REGION AND THEIR ANALOGUES IN THE PHANEROZOIC

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In this article, based on the analysis of the reconstructed lithologic composition of metapelitic and clay-carbonate carbon-bearing rocks of the Oskol'sk series in the Lower Proterozoic of the KMA region and reconstruction of the conditions of their accumulation, it is shown that their equivalent formations in the Phanerozoic are oil shales of the dictyoneme and kukersite types. The conclusion is drawn that the former accumulated in narrow, desalinated, shallow-water seas with hydrogen sulfide contamination and that the organic matter entering into their contamination and that the organic matter entering into their composition was of allochthonous-autochthonous origin. The latter were formed in desalinated bays or lagoons with good aeration of the waters and the source of the organics they contain was particularly autochthonous.

Within a broad spectrum of studies on Precambrian carbonaceous deposits, the problem of establishing their Phanerozoic analogues occupies a place of no small importance. This provides an opportunity for not only refining the accumulation conditions of Precambrian deposits rich in organic matter, but also tracing the evolution of untypical formations in geologic history and recognizing the specifics of conditions and phenomena in individual geologic epochs. Evoking special interest in this project is the comparison of formational conditions for Precambrian carbonaceous rocks and oil shales of the Phanerozoic, which have a single sapropel type of organic matter [14, etc].

In the present article, an attempt is made to decipher the conditions for the accumulation of graphite-bearing rocks in the terrigenous carbonate carbonaceous formation of the KMA's Oskol'sk series (based on the classification of N. A. Sozinov and S. A. Sidorenko [15]) and to compare them with such oil shales of the terrigenous-carbonate carbonaceous formation in the Ordovician in the northwest of Eastern European platform. The choice of these formations was not random. First of all, within the limits of the platform, they are the most similar with respect to age. Secondly, they are both the most representative of a number of carbonaceous formations: each has a considerable extent and high saturation in carbonaceous deposits, of which they contain rocks in both carbonate and clay series. Moreover, the rocks of the KMA carbonaceous formations within the structures studied underwent metamorphism of moderate degree (Ryl'sk structure: greenschist facies, Tim-Yastrebov: epidote-amphibolite), which in many ways facilitates the decipherment of their primary nature.

The carbonaceous rocks of the KMA Proterozoic are confined to the middle bed of the Oskol'sk series, a shale-carbonate complex 1000 m thick, which replaces a metasandstone-shale bed upward and is in turn covered by effusive or effusive-sedimentary formations. The carbonaceous rocks are represented by two varieties: quartz-mica shales (Ryl'sk, Tim-Yastrebov structures), sometimes with a minor admixture of calcareous material, and by rocks of primarily carbonate composition-mica-carbonate shales (Ryl'sk structure) and carbonate-amphibole rocks (Tim-Yastrebov structure), whose content of calcite-dolomite reaches 50-80%. The quantity of free carbon in the quartz-mica shales varied from 7-10% to 18-27%; in the carbonate rocks it usually does not exceed 4-5%.

The first of these are the best developed in the section. They make up a rather thick bed (up to 300 m) at the very bottom of the shale-carbonate complex and are sporadically developed in it and higher up in the section, where they constitute laminae up to a few dozen

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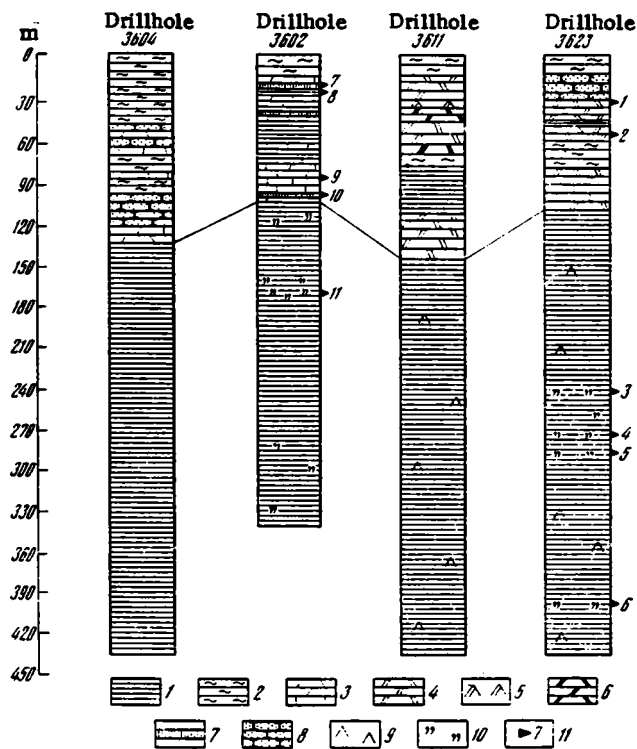


Fig. 1. Sections for deposits in the Oskol'sk series in the Tim-Yasterbov (holes 3611 and 3623) and Ryl'sk (holes 3604 and 3602) structures: 1) carbonaceous quartz-mica shales; 2) quartz-mica shales; 3) dolomites, limestones; 4) amphibole-carbonate rock; 5) amphibolites; 6) amphibole-carbonate carbonaceous rock; 7) dolomite-carbonaceous shale; 8) quartzites; 9) phosphate content; 10) carbonate content; 11) samples for isotope analysis.

meters thick and are not exposed along the strike. The carbonate carbonaceous rocks are of clearly subordinate significance in the section. They are in the form of thin laminae among the marmorized limestones and dolomites in the Ryl'sk structure and among amphibole-carbonate rocks in Tim-Yastrebov (Fig. 1).

The quartz-mica carbonaceous shales are massive, as a rule. A distinctly expressed banding is observed in parts of them, which is caused either by the uneven distribution of carbonaceous matter or by subparallelly oriented flakes of micaceous minerals. Characteristic of these shales are elevated concentrations (up to 10-15%) of sulfides (pyrite, pyrrhotite), and up to 25-30% of the rock mass in individual thin laminae. Throughout the entire thickness of the shales are encountered thin (fractions of a millimeter), black strata and nodules of carbonaceous-phosphatic composition, having sharp boundaries with the rocks surrounding them. The P_2O_5 content in the carbonaceous rocks does not usually exceed 1%; it reaches 1.5% in rare cases (Table 1).

The mineral constituent of the shales considered is mainly sericite and biotite (up to 60%), which make up the basic fabric of the rock, together with quartz and carbonaceous material. Occasionally, carbonate material is present in the mineral matrix, the amount of which may reach 5-6%. Feldspars are represented in the majority of cases by plagioclase, the content of which varies within broad limits. Individual horizons in the shales are rich in garnet.

Carbonaceous matter is uniformly distributed throughout the groundmass of the rock in the form of finely dispersed particles, forming dense growths with the mica minerals. Compact particles of graphite are noted only with veinlike quartzose segregates.

Recalculation of the original constituent of the carbonaceous quartz-mica shales, carried out by V. E. Zakrutkin [7] in accordance with O. M. Rozen's method, indicated that lithologically they are primarily silty-pelitic sands, in which the pelite fraction is hydro-

TABLE 1. Chemical Composition of Carbon-Bearing Quartz-Mica Shales in the Oskol'sk Series of the KMA, %

Component	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
SiO ₂	48,83	47,15	45,86	48,01	48,58	52,27	48,85	46,82	55,50	51,92	53,00	53,73	50,05	54,00	58,02
TiO ₂	0,52	0,57	0,66	0,74	0,47	0,79	1,09	1,04	1,09	0,57	1,30	0,68	0,86	1,04	1,34
Al ₂ O ₃	15,87	13,72	14,78	14,40	11,54	15,00	16,67	18,00	13,38	13,00	9,68	8,77	9,70	9,00	11,31
Fe ₂ O ₃	3,52	3,04	5,52	2,72	9,93	3,68	5,44	5,60	2,17	8,33	9,94	0,52	0,95	0,40	6,09
FeO	1,15	0,43	0,36	0,43	0,43	0,29	0,63	0,43	1,00	0,29	2,92	10,08	18,19	11,32	0,86
MnO	4,90	0,30	0,29	0,08	0,22	0,05	0,12	0,01	0,11	0,37	0,05	0,05	0,05	0,05	0,11
MgO	5,99	0,67	1,28	1,04	2,00	1,20	2,40	3,66	1,70	2,14	4,16	4,08	3,28	3,22	2,49
CaO	1,58	1,81	—	0,89	—	1,70	—	1,16	1,00	0,46	2,11	4,03	2,02	1,56	1,59
Na ₂ O	0,20	0,30	0,40	0,40	0,80	0,40	0,50	0,50	0,40	0,40	0,51	0,69	1,00	0,60	0,25
K ₂ O	1,94	3,32	3,32	3,48	2,94	3,68	4,22	4,42	3,28	3,58	3,21	2,22	2,83	4,80	4,90
S _{tot}	2,42	2,41	3,57	1,97	5,92	2,32	4,08	3,74	1,99	3,39	4,12	3,60	4,24	4,74	5,48
P ₂ O ₅	0,09	0,03	0,11	0,09	0,03	0,03	0,04	0,06	0,06	0,03	0,23	0,17	0,40	0,67	0,17
CO ₂	—	—	2,10	—	—	—	—	—	—	—	—	—	—	—	0,17
C _{org}	17,70	26,00	22,10	25,10	17,20	18,00	15,00	13,60	18,40	15,46	4,20	4,20	4,20	4,08	7,30
H ₂ O ^p	0,07	0,07	0,18	0,11	0,20	0,12	0,14	0,16	0,15	0,12	0,56	0,40	0,30	Not det.	—
Calcin ^g	0,35	0,37	0,05	0,66	0,20	0,64	1,29	0,85	0,74	0,36	Not det.	Not det.	Not det.	Not det.	Not det.
loss	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Total	100,13	100,19	100,58	100,12	100,46	100,17	100,57	100,05	100,97	99,96	99,75	100,27	100,35	100,38	100,04

Note: Tim-Yastrebov structure, numbers 1-10 (V. E. Zakrutkin's data [7]; Ry'lsk structure, numbers 11-15 (authors' data).

TABLE 2. Original Mineral Composition of Carbon-Bearing Metapelites and Metasiltstones in the Oskol'sk Series of the KMA, %

Mineral	Lithochemical recalculation data														
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Hydromica	43	39	44	32	65	41	46	55	42	74	25	23	21	23	16
Montmorillonite	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Kaolinite	27	20	20	23	9	18	19	22	18	—	10	6	5	6	16
Calcite	—	2	—	—	—	1	2	—	—	—	1	—	—	—	—
Dolomite	2	—	—	1	—	—	—	1	1	—	6	13	5	4	3
Magnesite	6	—	—	—	1	2	2	2	1	1	—	—	—	—	—
Iron hydroxides	1	—	3	—	5	—	2	1	—	2	12	8	17	8	6
Plagioclase	—	—	—	—	—	—	—	—	—	—	5	7	9	—	—
Microcline	—	13	11	17	—	11	14	10	3	—	7	1	6	23	18
Quartz	21	26	22	27	20	27	17	9	35	23	34	42	37	30	41

mica and kaolinite. Silty varieties of carbonaceous clay differ in their elevated content of the fine psammitic fraction (up to 45%), consisting of quartz and feldspar — microcline (Table 2).

The mica-carbonate shales are microbedded and microgranular. The microbedding was caused by the intermixing of laminae, with differing degrees of "dirty" organic matter. The carbonate material is dolomite and calcite and is from 50 to 80% of the rock volume. The remaining part is sericite, biotite, and carbonaceous matter. A decrease in the carbonate grains is noted, as well as an indistinctness in their boundaries, with increasing content of carbonaceous matter, which is present in the form of point inclusions in grains of dolomite and calcite and in the intergranular space. More rarely, carbonaceous particles are grouped in the form of vermicular accumulations along the bedding planes or in wavy bands cutting across the bedding.

The amphibole-carbonate carbonaceous rocks are usually medium-grained and consists mainly of carbonate (30-90%), amphibole (15-30%), and sericite (up to 15%). The carbonate is dolomite and calcite. The amphibole (tremolite and actinolite) forms radial and radiating aggregates and various growths (up to 12 mm in size). The carbonaceous matter is concentrated for the most part in zones of amphibole cleavage and in the interstices of carbonate grains. More rarely, it is encountered in the form of point inclusions of the latter.

The chemical composition of the mica-carbonate shales and carbonate-amphibole rocks is quite uniform (Table 3). According to the recalculation by the method indicated above [7], the original composition of the carbonaceous carbonate rocks showed that they contain a relatively high percentage of clay constituent (up to 10-20%), besides the carbonate component represented by calcite and dolomite. The clay minerals, according to the recalculation performed, are hydromica and montmorillonite (Table 4).

The carbonaceous matter in the rocks characterized above is of biogenic origin. We and other investigators have repeatedly presented proofs of this [6, 7].

Let us begin a reconstruction of the accumulation conditions for the carbon-bearing silt-pelitic metamorphic rocks with an analysis of the data based on the isotopic composition of C and O contained in their carbonates.* In this analysis, we shall use the diagram of Murata, Friedman, and Madsen (Fig. 2), in which the fields for marine and freshwater sands are shown on the coordinates $\delta^{13}\text{C}$ — $\delta^{18}\text{O}$, established on the basis of a generalization of a large number of data for the isotopes of carbonates of different ages and facies [20].

As seen from Table 5 and the diagram presented, the isotopic composition of the carbonates in carbon-bearing silt-pelites is considerably lighter: $\delta^{13}\text{C} = -6.3$ to -18.4% .

The occurrence of such a light isotopic composition for carbon could have generally been caused by two factors. First may have been the reducing conditions in which these rocks accumulated and which contributed to the accumulation of a large amount of organic matter and sulfides. In this connection, we shall point out the data available in the literature which confirm what has been stated. We have in mind the investigations of E. M. Galimov and V. M. Mazur on the Upper Jurassic and Cretaceous carbonates in Western Siberia, based on which it

*Analyses were carried out in the Laboratory of Isotope Geology, Academy of Sciences of the USSR, on a Varian MAT-250 instrument. The error in the carbon and oxygen determinations does not exceed $\pm 0.05\%$ which accordingly fall in the SMOW and PDB systems.

TABLE 3. Chemical Composition of Carbon-Bearing Carbonate Rocks in the Oskol'sk Series of the KMA

Component	1	2	3	4	5
SiO ₂	5,31	7,36	9,97	16,03	24,50
TiO ₂	0,10	0,05	0,28	0,30	0,27
Al ₂ O ₃	1,82	1,34	2,90	3,53	3,96
Fe ₂ O ₃	1,93	3,98	1,77	5,26	2,01
FeO	3,16	1,94	1,29	Not det'd	1,44
MnO	0,36	1,40	1,08	0,50	1,76
MgO	18,69	3,60	17,47	3,58	14,28
CaO	23,91	40,34	27,36	34,11	19,04
Na ₂ O	0,10	0,20	0,18	0,24	0,06
K ₂ O	0,09	0,09	—	0,32	1,52
S _{tot}	1,50	0,24	1,42	0,18	1,40
P ₂ O ₅	0,08	0,06	—	Traces	0,43
CO ₂	37,46	30,26	34,92	24,30	25,40
C	4,50	5,60	1,70	7,90	4,40
H ₂ O _{org}	0,62	0,91	0,11	0,03	0,05
Calcin.loss	0,85	2,28	Traces	3,99	3,00
Total	100,48	99,65	100,46	100,27	100,52

Note: Tim-Yastrebov structure, numbers 1-4 (V. E. Zakrutkin's data), Ryl'sk, number 5.

was shown that similar values (up to -10‰) are characteristic of conditions with hydrogen sulfide contamination of the waters. Galimov comes to the conclusion that the occurrence of hydrogen sulfide contamination leads to a low rate of isotope exchange and contributes to the establishment of an exchange cycle between the carbon in the carbonates and the carbon of isotope-light carbon dioxide, which evolves as a result of decomposition of organics [4, 5].

Secondly, one reason for these values might be the influence of fresh continental waters upon the sedimentation medium. With this hypothesis, the fact that a majority of the figurative points for these rocks (three out of five) fall in the field of freshwater sediments on the representative diagram is of interest (samples 3, 4, and 8: $\delta^{13}\text{C} = -6.3$ to -16.6% , $\delta^{18}\text{O} = 18.3$ - 20.1%), while two samples are found in the immediate vicinity, not falling within it only as a result of the light isotopic composition of carbon compared with that established for the freshwater formations (samp. 5 and 6: with $\delta^{13}\text{C} = -17.0\%$ and -18.3%).

Such a point distribution, in our view, deserves attention, if only for the reason that V. E. Zakrutkin proved a lake origin for these sediments, based on the ratio of accumulation coefficients for elements in the nickel and vanadium groups and on a number of other indicators.

We are not eliminating the possibility of carbonaceous silt-pelite accumulation under lake conditions, but we nevertheless prefer the point of view that they accumulated in freshwater seas based on the following factors. We primarily point out the existing dependence, sufficiently evident although not entirely distinctive, of C_{org} content upon the size of the clay constituent (Fig. 3), which permits us to consider not only the participation of continental waters in the formation of the reservoir medium to be authentic, but also permits the statement that this discharge transported to some degree or other, into the reservoir, allochthonous organic matter, which made up a considerable portion of the total organic matter accumulated in the sediments. And since extensive vegetation was absent on the land, it must be assumed that the organic matter transported was aqueous humus from lakes, which formed from lower freshwater algae, and that the final discharge basin was the sea.

There are also other data which point to the fact that the basin was marine: the rather stable position, at the bottom of the section, of the shale-carbonate complex of a thick bed of silt-pelite carbonaceous deposits over the considerable territory of the KMA, maintaining their lithologic composition, as well as the presence in them of carbonaceous-phosphate concretions. The formation of phosphorites is associated with stagnant waters and with a calm tectonic regime [2]. It must be supposed that these conditions also occurred at the time the carbonaceous silt-pelites accumulated in the Oskol'sk series in the KMA. The marine basin, judging from all this, was small, of closed or semiclosed type, slight freshened due to abundant continental runoff.

TABLE 4. Original Mineral Composition of Carbon-Bearing Carbonate Rocks of the Oskol'sk Series of the KMA, %

Mineral	Lithological recalculation data				
	1	2	3	4	5
Hydromica	4	2	3	8	19
Montmorillonite	6	8	10	1	—
Kaolinite	—	—	—	8	—
Calcite	—	61	6	47	—
Dolomite, magnesite	82	14	69	13	47
Iron hydroxides	5	9	4	7	3
Plagioclase	—	—	—	—	—
Microcline	—	—	—	—	11
Quartz	3	6	8	10	20

Terrigenous organics, carried along with this discharge in significant amounts, contributed to the occurrence of hydrogen sulfide contamination, which in turn might have led to even lighter isotopic composition of oxygen in the carbonates. Evidently, this might also explain the extremely low values for $\delta^{13}\text{C}$ in samples 5 and 6.

The humid climate, which was established from the presence in silt-pelitic sediments of large quantities of kaolin, contributed to the occurrence of lakes on the continent, since it is well known that under the conditions of a hot humid climate and a comparatively level relief, weathering takes place more intensively and is accompanied by the formation of very stable clay minerals of the kaolinite group [12].

The processes of chemical weathering actively occurring under conditions of a humid climate apparently contributed to the fact that nutritive substances fell into the sedimentation basin in large amounts, which led to the development of very simple phototropic organisms which made up the autochthonous portion of the organic matter in the silt-pelitic metamorphic rocks. Actually, they were blue-green algae, since the assemblage of amino acids developed in these deposits is similar to those in such microorganisms [7].

The carbonaceous silt-pelites of the KMA in the section of the carbonaceous formation in the cis-Baltic Ordovician is, based on its lithologic composition, very similar to Dictyonema shales, in which a hydromica-kaolinite composition is also characteristic in the clay particles and a quartz-feldspar composition for silt-size grains, which may reach 30-50% of the rock by volume [8].

We may consider, with a definite degree of certainty, the conditions of the accumulation environment to be essentially similar to both the carbonaceous metasilt-pelites of the KMA and Dictyonema shales. This means a near-bottom hydrogen sulfide contamination and constant or periodic freshening of the basin, caused by an influx of continental waters bearing terrigenous organic matter. In support of the former is the high content of organic matter, even for metasilt-pelites, and in support of the latter, the presence of humic acids in the organic matter of the Dictyonema shales, the amount of which sometimes reaches 40% of the organic matter in these shales [18], and what is more, the increases in the quantity of organics with increasing alumina (Fig. 4). The Dictyonema shales were laid down in an epicontinental ocean-bay (gulf) which was always being freshened.

The difference between the two apparently lies only in the rates and duration of accumulation of the sediments being compared. The accumulation of silt-pelites in the Oskol'sk series took place in a linearly extending (seam) downwarp with features of both geosynclinal and platform development — a paleoaulacogen [11] or marginal downwarp [7], which defines their considerably greater thickness in comparison with such Dictyonema shales (1-7 m), which accumulated under typical platform conditions.

Carbonate formations of the KMA Oskol'sk series in the areas studied had, judging from the data on $\delta^{13}\text{C}$ in the carbonates, somewhat different accumulation conditions. The carbonate rocks of the Ryl'sk structure, including the carbonaceous ones, fall in the range of marine sediments, based on the $\delta^{13}\text{C}$ values. It is characteristic here that they all have negative values, varying mainly in the range of -1.4 to -2.3‰ (see Fig. 2 and Table 5). According to Parker and Keith [19], who established the sequential process of the isotopic composition of carbon becoming lighter in the organic carbonates, from the open ocean toward the shoreline band and the relationship between the isotope composition and the water salinity, the range

TABLE 5. Isotopic Composition of Carbonates in the Oskol'sk Series, KMA

Rock	$\delta^{13}\text{C}$, ‰ (PDB)	$\delta^{18}\text{O}$, ‰ (SMOW)
Tim-Yastrebov structure		
Carbonate-amphibole rock	-7,6	24,7
Same	-10,7	20,5
Carbonaceous quartz-mica shale	-16,6	19,8
Same	-10,4	18,3
"	-18,4	15,3
"	-17,0	15,2
Ryl'sk structure		
Dolomite-carbonaceous shale	-2,3	20,6
Carbonaceous quartz-mica shale	-6,3	20,1
Dolomite	-0,5	21,2
Dolomite-carbonaceous shale	-2,6	19,7
Marmorized dolomite	-1,4	19,7

of values presented is characteristic of lagoons and marginal bays (-1.0 to -3.2‰) with water salinity from 18 to 34‰.

The probability of a biogenic nature for the carbonates in the carbonate-clay formations of the KMA is rather high. They might have been very simple single-celled organisms of the coccolithophorid type. Forms similar to these organisms have been noted repeatedly in the Precambrian.

The carbonate-amphibole rocks of the Tim-Yastrebov structure have lower carbon values: $\delta^{13}\text{C} = -7.6$ and -10.7% . The nature of these values may be different. Without taking into consideration the processes which might have caused such a lightening of the carbon isotope composition, we shall point out that one of the reasons could have been the freshening of the basin, more intense than in the Ryl'sk structure, in other words, that the carbonate formations of the Tim-Yastrebov structure were laid down in areas closer to the continent.

As is well known, the runoff of fresh waters into the marine environment causes stratification of the waters and the creation of a biological disequilibrium, which in the final analysis leads to a vigorous flourishing of the plankton, which probably serves as the major source of organic matter in these rocks.

The closeness of $\delta^{13}\text{C}$ values in carbonaceous and noncarbonaceous varieties of carbonate rocks in the Ryl'sk structure is related to the fact that the influence of allochthonous light-isotope carbonates upon the formation of carbonate isotope composition, if it did exist, was extremely insignificant. This may serve as an indirect proof of the autochthonous character of the organics in the carbonate rocks, the shallow-water nature of the basin, and the good aeration of the waters in it.

It is characteristic that the isotope ratios $^{18}\text{O}/^{16}\text{O}$ for all the carbonate rocks is maintained and is comparable on the whole with those considered above for the silt-pelites.

The climate at the time the carbonaceous carbonate formations accumulated was arid, since in a climate becoming arid, when the weathering processes are retarded, kaolin disappears completely from the composition of clay products and the widespread development of hydromica and monmorillonite takes place [12], i.e., those associations of clay minerals are formed which make up the clay portion of these formations.

The absence in the bed of large-clast deposits and, on the other hand, the widespread occurrence, based on lithochemical recalculations, of poorly sorted silty, essentially clay and carbonate deposits with characteristic bedding of the ribbon type provides a basis for considering the entire shale-carbonate bed of the KMA Oskol'sk series to be primarily lagoonal formations or formations of marginal portions of the sea.

In the Ordovician section of the cis-Baltic region, very close to the carbonaceous clay-carbonate rocks of the KMA are the kukersite shales. The mineral part of these, in addition to carbonates (calcite, and more rarely dolomites) is hydromicas and micas and characteristically does not include kaolin [3]. The kukersites accumulated under the conditions of an arid climate [17]. As for the type of basin in which they were laid down, there is no single opinion among investigators on this matter. Thus, M. D. Zaleskii [8] considered them formations of the near-shore part of the ocean or of near-shore lakes periodically overrun by the

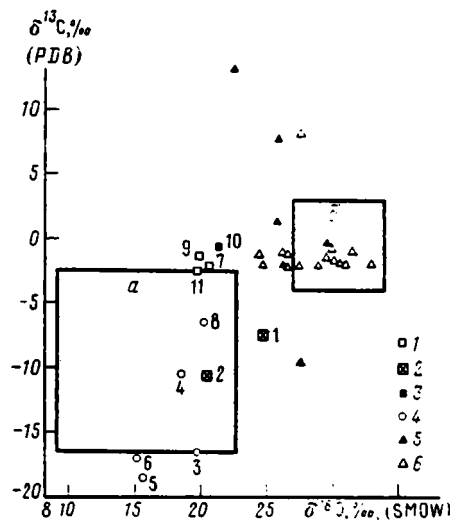


Fig. 2. Interrelationships between isotopic composition of carbon and oxygen in carbonate rocks of the Oskol'sk series in the KMA and the shale-bearing bed of the Baltic Ordovician (a: freshwater sediments, b: marine sediments). 1) Dolomites, 2) carbonate-amphibole rock, 3) dolomite-carbonaceous shale, 4) quartz-mica shale, 5) kukersites, 6) limestones in the interkukersite layers and limestones contained in the kukersites in the form of lenses and laminae. Numbers on the graph: sample numbers.

sea. N. M. Strakhov and D. B. Nalivkin [13, 16] and a whole series of other investigators supposed that the accumulation of these shales took place under open ocean conditions and at a great distance from shore.

As the study indicates of isotope composition for kukersite carbonates and the limestones associated with them in the Estonian deposit, Zalesskii's point of view is preferable. The point is that data on the isotope ratios of carbon and oxygen confirm the participation of continental waters in the formation of the accumulation environment for these rocks. In the first place, the isotope composition of oxygen in the kukersite carbonates indicates this. As is evident from Fig. 2, practically all the samples of kukersite fall in the range of marine sediments, according to their $\delta^{18}\text{O}$, but they are subgrouped in the same area which is closest to the $\delta^{18}\text{O}$ of freshwater carbonates. In addition, the $\delta^{13}\text{C}$ values for the limestones, maintained in the interval of -1.45 to -2.45% , are also evidence of this, since this interval, as was indicated above, is characteristic of lagoons and marginal bays with a water salinity from 18 to 34‰.

As seen from Fig. 2, half of the six samples investigated for kukersite fell, as has been expected, within the $\delta^{13}\text{C}$ range of marine sediments, and the other half, in comparison, have an "anomalously" light or "anomalously" heavy carbon composition, which without a doubt excludes any original nature for them. Their diagenetic nature can evidently also be explained satisfactorily by the isotope-carbon interaction of organic matter and carbonate, which occurred in the closed cycle of the labile $\text{CH}_4\text{-CO}_2$ system in diagenesis while utilizing a large quantity of the organic mass contained in the rock [4].

Planktonic blue-green algae, which Zalesskii determined to be *Glaeocapsomorpha prisca* Zal [8], served as the source of organic matter in the kukersites.

Finally, the majority of investigators consider that hydrogen sulfide contamination of the waters did not occur during the deposition of the kukersites.

Thus, from what has been stated, it may be concluded that the clay-carbonate rocks of the KMA's Oskol'sk series are similar to the kukersite shales of the Ordovician not only in lithologic composition but in conditions of formation.

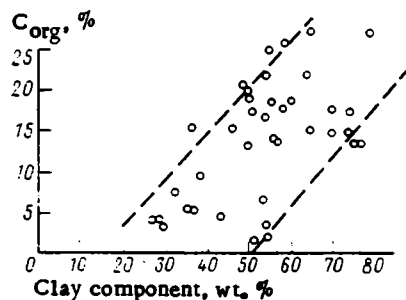


Fig. 3

Fig. 3. C_{org} content as a function of the clay component in the mineral matrix in carbonaceous silt-pelites in the Oskol'sk series, KMA Proterozoic (drawn on the basis of data from V. E. Zakrutkin [7] and the authors).

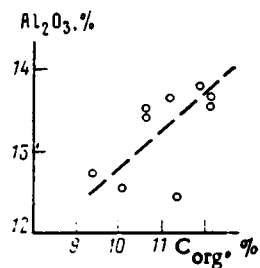


Fig. 4

Fig. 4. Al_2O_3 content as a function of C_{org} in Dictyonema shales of the Baltic Ordovician (drawn on the basis of O. T. Kirret's data [9]).

In conclusion, the following deductions may be presented.

1. The carbonaceous silt-pelites of the Oskol'sk series in the KMA are formations of narrow, shallow-water and freshened seas, extended over great distances, in the near-bottom portion of which hydrogen sulfide contamination was developed. The organic matter in these formations is of allochthonous-autochthonous origin, in which the allochthonous portion is, to all appearances, aqueous humus from the lakes around the marine reservoir, while the autochthonous portion is autotrophic organisms of the bluegreen algal type. The climate on the nearby land was humid, contributing to intense chemical weathering and establishing in the sedimentary basin the maximum amounts of biogenic elements.

2. The clay-carbonate metamorphic rocks of the KMA Proterozoic accumulated under near-shore-marine conditions — freshwater bays or lagoons with good water aeration. In the drainage basin areas, an arid climate predominated. The source of organic matter in the rocks was autochthonous. It is most probable that they were planktonic organisms, which actively multiplied in a period of biological instability in the reservoir, caused by the influx of fresh continental waters.

3. Based on the lithologic composition and the conditions of formation, the carbonaceous silt-pelites of the KMA Oskol'sk series are similar to Dictyonema shales, and the carbonaceous-clay-carbonate metamorphic rocks are similar to the kukersite shales, which confirms, in our view, the essential similarity of causes evoking the rise of circumstances favorable for the accumulation of carbonaceous rocks with a sapropel type of organic in the European portion of the USSR at the end of the Proterozoic and the beginning of the Paleozoic.

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Principles, structure, and possibilities are discussed in this article for rock-chemistry methods and their applicability to reconstructing the material nature and formation conditions of sedimentary formations in the Precambrian.

In association with the practical and theoretical significance of the sedimentary (and volcanic-sedimentary) Precambrian, the reconstruction of objects of this type is being conducted in many different directions, using a broad spectrum of rock-chemistry methods. Among the latter, a role of no little importance is being redirected toward the methods of rock chemistry. The purpose of the present article is to give a correct procedural evaluation of their applicability to the reconstruction of the nature of Precambrian sedimentary rocks.

The structure of rock-chemistry methods may be represented schematically in the following form (Fig. 1).[†]

As is evident from the sketch, rock chemistry methods concern two types of information: chemical composition and standard geological information and the criteria which define the sphere of their applicability. The criteria have a twofold nature, thereby reflecting the twofold nature of the information carried.

It is not hard to be convinced of the fact that the methods of rock chemistry "begin" with the introduction of standard geological information, and since the latter has a temporal character, it must be introduced separately for each geohistorical epoch...the Phanerozoic, Proterozoic, Archean, etc. Knowledge of standard information is unthinkable without studying the features of sedimentogenesis for each geohistorical epoch. Consequently, in order for rock chemistry methods to be true "to life," there must be other methods, nonrock-chemistry methods, with whose aid the most important features of exogene processes might be revealed, in particular for the Precambrian, and on this basis standard information developed.** The complication consists of the fact that at the present time, such methods do not exist for the reconstruction of the majority of objects in the sedimentary Precambrian, not to speak of any verification of the results of similar reconstructions in practice, i.e., by independent methods. Keeping this in mind, let us trace how rock chemists are attempting to overcome this and other difficulties standing in the way of applying the method they have proposed.

Reconstructing the conditions for sedimentogenesis and volcanism in the early Precambrian by rock chemistry methods, A. A. Petrovskii emphasizes, is based on the following two principles: 1) the *qualitative* similarity of Precambrian and Phanerozoic processes and 2) the *preservation* of the main features of chemical rock composition during regional metamorphism. "Recognition of the principles given," continues this author, "opens up the way to understanding the primary nature of *deeply* metamorphosed sedimentary and volcanic rocks which have lost their

*With the publication of this article, the Editorial Board is initiating a broad discussion of the legitimacy of procedures for petrographic recalculations for metamorphic rocks; we call upon all those so desiring to take part in the discussion of this problem on the pages of our journal.

[†]In the sketch presented, geohistorical time is intended (the Phanerozoic, lower Proterozoic, etc.).

**At the present time, it has been possible to bypass the problem of standards, particularly in the case of element-geochemical methods applied to Precambrian iron formations. There is a circumventing path: using those properties of matter and the environment which do not depend on the coordinates of geohistorical time [4, 6, etc.].

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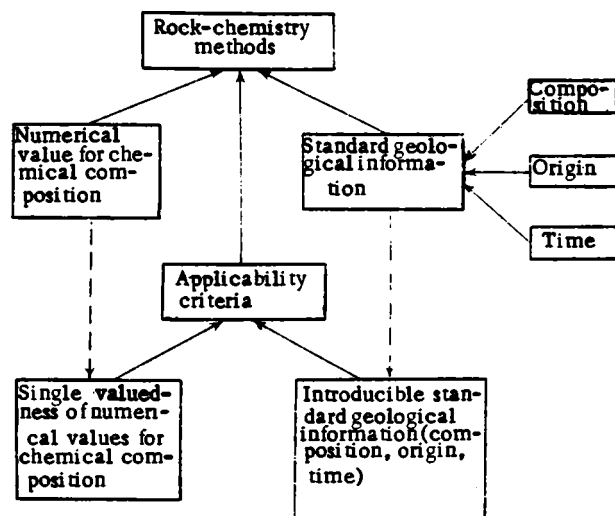


Fig. 1. Structure of rock chemistry methods.

original aspect and mineral composition, and a path to "open" comparison of the chemical composition of *typical** rocks related to different Precambrian and Phanerozoic stages of development of the planet...the use of chemistry for systematics and recognition of the primary nature of metamorphosed primary sedimentary and volcanic formations is a *very universal and common approach*...("The invariable use of the entire assemblage of geological information is proposed based on objects studied, as a necessary condition for proving the results obtained"[†]) [17, p. 6]. The history of the revelation of these principles is extremely instructive, and it is advantageous to dwell on this in more detail.

PRINCIPLE OF QUALITATIVE SIMILARITY OF PRECAMBRIAN AND PHANEROZOIC PROCESSES

The first principle, as Predovskii himself states [17, p. 3], is no other than that conclusion established by A. V. Sidorenko, "on the prime similarity of processes and conditions of Precambrian and Phanerozoic exogene rock formation." In association with this, it is pertinent to note that since Sidorenko drew the conclusion [19, 20] that Predovskii's "very universal and general approach" appeared [15 and others], apparently less universal and general approaches are at its basis, and consequently, it is needed in the most careful proofs. Since Sidorenko's conclusion cited above is at the basis of Predovskii's rock-chemical method, the results of Predovskii's investigations may not serve as a criterion for the truth of Sidorenko's conclusion itself. Meantime, in Predovskii's works, we read the following: "As a result of the investigations carried out, the truth of an important hypothesis formulated by Sidorenko is once more indicated in highly detailed material [19, 20], the position concerning the essential similarity of sedimentation processes and sediment composition in the Precambrian the Phanerozoic. All the geochemical and facies features of the metasediments of Pechenga, without exception, may be qualitatively correlated with the features of Phanerozoic sediments of a different stratigraphic and geotectonic position" [16, p. 129].

But this is not the sum of the matter. We must also turn our attention to the fact that the "truth" of one of Sidorenko's important hypotheses is indicated in study materials from the Middle Proterozoic [16, p. 4] of the Pechenga complex, while verification of the truth of Sidorenko's conclusion must extend over the entire Precambrian. And it is in the lower Proterozoic itself that the most substantial differences begin to appear between the Precambrian and the Phanerozoic (the Precambrian iron formations of Krivoi Rog, the KMA, and other

*The question arises as to how the a priori investigator can know whether what he is comparing is typical or atypical.

[†]From the procedural point of view, any information concerning natural processes and objects is divided into external and internal (genetic): thus, what kind of information is it a question of here? If it is external, it does not change the essence of the matter; if it is internal, then with what are the rock chemistry methods associated here?

places, the uranium-bearing conglomerates of the Witwatersrand type, Blind River, and other locales, etc.).

One may judge what the subsequent application by Predovskii of his first principle is leading to from the following statement of his: "The example presented [concerning the review of the conclusion of supporters of the allochemical" character of regional metamorphism — I. B.] is a convincing illustration of Sidorenko's repeatedly expressed opinion that knowledge of the nature of the metamorphic complexes in the Precambrian is kept in check to a considerable degree by procedural reasons and by the underestimation of the role of exogene factors and processes in their formation" [17, p. 5]. From the point of view of this author, this example illustrates something completely different, namely that Predovskii is not in harmony with the logic of scientific knowledge. Indeed, it is hardly necessary to point out that to the present time, Precambrian conditions (atmosphere, hydrosphere, etc.) have not been preserved anywhere on the earth in their original form and that the products of exogene processes of Precambrian age could have occurred only in metamorphosed form. Therefore, we can only judge whether exogene processes took place generally in the Precambrian and if they did, on what scale, etc., "through" the reconstruction of metamorphosed rocks, i.e., exposing their premetamorphic and original nature, separating from them a number of the products of exogene processes and evaluating their composition, distribution, etc., and not the reverse, as Predovskii thinks and accomplishes in practice.

In addition to what has been stated, one more example of Predovskii's scientific approach to the analysis of natural processes is presented [16, p. 25]: "The rose or red *color* of the deposits [speaking of the deposits in the second bed of the Pechenga complex — I. B.] and the *absence* of a large quantity of clay matter tells of a hot dry climate of the arid type." But in such a case, one part of the Precambrian iron formations must have belonged to deposits which formed in a "hot dry climate of the arid type"...that part which is characterized by a "rose or red color and in which a large quantity of clay material is absent; and what about the remaining portion of the Precambrian iron quartzites, in which a large quantity of clay material is also absent, but the color is not "rose or red," but is gray? Furthermore, how is the climate interpreted in those cases in which rose or red strata in the iron quartzites are replaced by gray ones along the strike, within a single sample (the New Krivoi Rog, Greater Gleevatka, and other deposits and the Krivoi Rog basin)?

In association with the present attempt of rock chemists to transfer the patterns of sedimentogenesis and volcanism in the Phanerozoic to the Precambrian, we must turn our attention to an extremely unusual approach, using which several of these scientists are obtaining similarities in geological processes and formations of historically different ages. This matter concerns Predovskii's exclusion [15, p. 5] "of deposits which are specifically rich in iron, manganese, phosphorus, etc." (among which fall, primarily and naturally, the Precambrian iron quartzites) from the sphere of the rock chemical method and the problems associated with its applicability.* In uniting all the iron ores in "formations specifically enriched in iron," Predovskii first of all camouflages the elements of obvious and clear evolution in natural formations (compare, for example, the near-shore oolitic iron ores of the Phanerozoic and the chemical iron quartzites of the Precambrian which are displaced toward the pelagic zone), and secondly, by linking the iron ores with phosphorus, manganese ores and so on, this author thereby masks the exceptionally important indicator role of iron. Before excluding "formations specifically enriched in iron," it is necessary to explain what they represent and whether they bear any information about the external environment, etc. If we approach the iron ores just from this point of view, and turn our attention to the fact that the mineral forms of iron are the most important indicators of oxidation-reduction conditions in all geological formations without exception (not just in oxidative-reductive ones!), that is one thing, to say nothing of the extremely wide distribution of iron quartzites on all the continents (on the Kola Peninsula, where Predovskii worked in particular, the large well known Olenogor deposit, and more than a dozen medium-sized and small deposits of iron quartzites, as well as several dozen occurrences of iron quartzite in various portions of them [9 and others]), the complete irregularity (mechanicity) of Predovskii's operations is clear. By excluding "formations specifically enriched in iron," i.e., excluding the indication of oxidation-reduction conditions in the Precambrian, Predovskii thereby opened the way, not to "recognizing the original nature of the deeply metamorphosed sedimentary and volcanic rocks"

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Let us consider several of the most negative instances in Neelov's monograph [13]. In the introduction, where this author has to provide a basis for expediency in developing a rock chemical classification, we learn that "during regional metamorphism, in its early stages in sedimentary and volcanic rocks, the most important indications of their original nature disappear. First, the mineral composition of the rocks is altered and signs of sedimentary and volcanic textures disappear and sometimes even structures. As early as the greenschist facies complications arise in the determination of the original grain-size composition of sedimentary rocks. Therefore, together with geological and mineralogical methods of reconstructing the original nature of the metamorphic rocks...rock chemical and geochemical methods have the greatest importance" [13, p. 3]. These complexities disappear in the final chapter, and "investigations based on the first method [i.e., the methods of comparing compositions with a lithologic control of the same time — I.B.] have yielded unambiguous results, which confirm that up to the zone of ultrametamorphism, metapelites, metasandstones, and metabasic rocks experience no substantial or regularly patterned changes in the content of the major elements" [13, p. 73].

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There is no doubt that a lithologic control is necessary in presenting such studies. But its problems are not just reduced to excluding the possibility of linking, in the analysis, sample rocks belonging to different grain-size groups or even to different ages or formationally different metamorphic complexes [13, p. 74]. In this understanding of the problems of lithologic control, the extremely important aspect of sequence in mineral formation is avoided, which is necessary in order to find out what stage of paragenesis the minerals (or mineral) are at which we are analyzing (progressive — regressive), and for minerals of foreign stages of mineral formation not to fall among the samples being analyzed. Only in this case can an objective solution to the problem be provided concerning the preservation of this or that feature of the chemical composition in sedimentary and volcanic rocks in the process of regional metamorphism. Moreover, by virtue of the reasons mentioned above, the truth of such reconstructions must be mutually monitored by independent methods of investigation. However, as we already considered in the beginning of this article, for the majority of metamorphic rocks at the contemporary level of geological science, the observance of these requirements cannot be fulfilled. Consequently, for the majority of metamorphic rocks, *objectivity cannot be provided in conclusions regarding the character of the chemistry in the processes of regional metamorphism.*

Besides seeking out paths and possibilities for solving problems of time in application to metamorphic rocks, Neelov proceeds along the line of selecting more accessible, but erroneous, criteria for the isochemistry of processes in regional metamorphism. "One important indicator of low element mobility during regional metamorphism" writes Neelov, "is the distinct banding in metasedimentary beds, reflecting very minor alterations in the original composition of the strata, with the preservation of both sharp and gradual transitions from layer to layer" [13, p. 75]. Here the author makes a procedural error, in that he employs indications belonging to the category of spatial indicators (external), distinct banding being nothing other than a feature of the spatial distribution of matter, as a criterion for genetic (internal) indications, i.e., the mobility of the elements.

A consequence of the procedural position assumed by Neelov has been a purely formal approach to the characteristics of Precambrian iron formations, which, in contrast to Predovskii, he introduces into his rock chemical classification [13, Figs. 3, 8]. This formal approach appeared first of all in the selection of primary forms of ore deposits (oxides... iron carbonates), which is not at all well founded, other than in references to the formal work of Lepp and Goldich [21], and secondly, in the subsequent description, in Neelov considering the Precambrian iron formations either together with young carbonate-clay-iron formations as an extratemporal rock-chemically unique group, or combining the siderites of Precambrian iron formations and younger deposits (Jurassic oolitic ferruginous sediments of England, bituminous shales of the Green River formation in Wyoming, Colorado, and Utah, etc.) again in an extratemporal rock-chemically unique supergroup (in Neelov's classification, iron carbonates are considered within the "c" parameter) [13, pp. 59, 60 and elsewhere].

There is also nothing principally different in the work of H. de la Roche [7]. Having worked out Predovskii's rock chemical methods, de la Roche and Neelov have introduced a series of limitations to their applicability and apparently, not noticing this, they have done everything necessary, in essence, for their simultaneous liquidation. Let us evaluate some of these limitations.

Thus, according to de la Roche [7, p. 263], before employing rock chemical classifications and the corresponding methods, it is necessary to introduce corresponding *standard* information. The applicability of modern standard systems is limited in time and cannot be extended to the Precambrian (extratemporal application of the standard systems reduces any scientific analysis of natural systems and processes to a mechanistic analysis). As for the possibility of explaining the standard systems of the Precambrian by nonrock chemical methods, this is still extremely limited.

From the number of objects to which the rock chemical methods are applicable, Predovskii [15, p. 8] and Neelov [13, p. 12, see note] excluded the rocks which had undergone obvious input or output of matter. Since the investigators could not know a priori which rocks had undergone significant influx or efflux of matter and which had not, each sample studied had to be subjected to a preliminary analysis for the purpose of throwing out those which did not satisfy the given requirement. This analysis was a cycle of sample investigations by nonrock-chemical methods and could not avoid including reconstruction of their premetamorphic nature, because without knowing what these rocks were and what their mineral and chemical compositions were, it is impossible to evaluate the nature and degree of influx-efflux of matter in the process of metamorphism. At the present time, such (nonrock-chemical) have been developed, for instance, for reconstructing the premetamorphic nature of ore matter in Precambrian iron formations [2-6, 22, etc.]. Consequently, even in the process of throwing out samples using nonrock-chemical methods, we are obliged (although we still cannot always) to find the premetamorphic nature of the samples studied. In such a case, why are rock chemical methods needed?

QUESTION OF ISOCHEMISTRY IN THE PROCESSES OF REGIONAL METAMORPHISM

Along with the developers of rock chemical methods, more and more geologists have been promoting notions of the isochemistry in the processes of regional metamorphism, geologists who are working in the area of sedimentary Precambrian geology. The extension of these views favors, on the one hand, the undoubtedly true criticism addressed by a number of geologists, of an allochemical trend (L. d'Argues [10], S. M. Aleshin [1], and others) and on the other hand, numerous publications, from articles to monographs, in which the isochemistry of the processes in regional metamorphism is, so to speak, proven in number and degree.

And in spite of this, the overall state of the problem treated here still gives an unsatisfactory impression. It begins with the general statement of the problem. Actually, what is this *isochemistry* of regional metamorphic processes, if we go beyond the framework of narrowly specialized thought? Isochemistry is nothing but a *constant*; it proceeds from the *constancy of natural processes*...this means assuming that *matter can be retained in both its movement and development*. In this connection, it is appropriate to turn our attention to how the problems of studying matter are stated (one of the forms in which it occurs is that of regionally metamorphosed rocks) in a generally scientific (philosophical) aspect. This concerns, in particular, practice, as a criterion for the objectivity of our knowledge. As is well known, one of the properties of this criterion is its "nondeterminateness," but nondeterminateness only to such a degree as to not allow human knowledge to be transformed into an "absolute," also being provided with the infinite nature of the very process of understanding. What is this isochemistry of regional metamorphic processes? It is no other than an "absolute," like ultimate knowledge. If scientific conclusions objectively reflect the essence of geologic phenomena and processes, they cannot be a hindrance to establishing investigations at a higher level in the infinite process of understanding. But if the process of regional metamorphism is an isochemical process, what problems may be stated on the basis of this conclusion, which would be more in-depth and universal investigations, i.e., of a subsequent level of understanding? To come out with this as a foundation means to remove from the sphere of scientific knowledge a large, extremely important (especially for understanding the Precambrian), and still imperfectly studied area in geological science. To prove isochemistry (as a general case) means to indicate with knowledge in the investigations presented whatever was not considered and wherever mistakes were made. We shall present examples of a number of these, to which Predovskii and Neelov refer.

Example 1. In a short article by S. B. Lobach-Zhuchenko and others [11], the object of study was the chemical composition of metamorphosed effusive-sedimentary rocks and flysch of the Ladoga Formation in the Baltic shield (absolute age 2300-2500 million years). The degree of rock metamorphism varies from epidote-amphibolite facies to granulite. In the southwestern part of the cis-Ladoga region, intense migmatization and granitization appeared. The authors' conclusions are reduced, in particular, to the following positions.

1. Within the epidote-amphibolite and amphibolite facies, the regional metamorphism of the rocks in the Ladoga Formation proceeded isochemically without directed alteration of the contents of SiO_2 , FeO , MgO , CaO , and Na_2O and K_2O . The exception is the water content and degree of iron oxidation (Fe_2O content varied from 0.85 to 1.05%).

2. Ultrametamorphism of the Ladoga Formation, which leads to the formation of an essentially plagioclastic rock complex, proceeded under conditions of a closed system for the major rock-forming oxides.

Without going into a discussion of a number of deviations from the isochemistry of processes in regional metamorphism and ultrametamorphism, for which Lobach-Zhuchenko et al., give one explanation or another, or under which conditions the deviations occurring may be considered to be substantial and which not, we shall look at several principally important positions in their work. Of these, first of all, is the method of sampling the rocks in the Ladoga Formation. "The chemical composition" write these authors, "was determined for average samples, obtained by the method of areal sampling in a large portion of the territory... The samples were set up separately for rocks which were different in composition (gneisses, amphibolites, granites, etc.) for each subzone of metamorphism.* The samples...were selected...over a grid (for the metamorphic rocks, 2×2 km...)...When the outcrop turned out to be composed of two or more rocks, the sample taken consisted of all the representatives of the rocks, taken in corresponding proportions. These points were summed into a group of rocks called 'mixed rocks' in Table 1." And furthermore, "such a sampling method has been used previously in computing the mean chemical composition of the Canadian shield (reference to the work of Eade et al. 1966)" [11, p. 356]. Actually, if the aim of the investigations is simply to calculate the average composition of the Canadian shield (or an object even less large), this method might possibly be valid. But it is an entirely different matter in the work of Lobach-Zhuchenko et al.,...the behavior of petrogenic elements in a *process*! This means that the factor of time emerges in the first plan of attack! The main thing in sampling becomes not the selection of samples over a grid, etc., but selection of samples which satisfy definite requirements on the basis of a reconstruction of the sequence of metamorphic mineral formation in conjunction with a lithologic control. The following enter into the latter problem: 1) making

*No extratemporal subzones of metamorphism exist.

sure that only those samples are analyzed which had at the time of metamorphism the same or a sufficiently similar chemical and mineral composition, and 2) throwing out the samples in which minerals from foreign stages of mineral formation were present. Finally, if we stick to all the rules, all this in turn must be mutually controlled by independent methods of analysis.

Studies of such a nature, with the rare exception, cannot be carried out under laboratory conditions, and under field conditions, it cannot even be considered. Thus, for instance, in general what lithologic control at the modern level of knowledge can deal with sampling of rocks in zones of ultrametamorphism?

Since, judging from the description presented, such work has not been done. The conclusions of Lobach-Zhuchenko et al. [11] regarding the isochemistry of processes in regional metamorphism have the meaning of hypothesis, which may turn out to be false to an equal degree.

Finally, one more note involves these authors' conclusion [11, p. 360] that "ultrametamorphism of the Ladoga Formation...took place under conditions of a closed system for the major rock-forming oxides." From a comparison of the average compositions of rocks in the zone of ultrametamorphism and outside of it, it is impossible to draw a conclusion regarding the open or closed nature of natural systems. The fact is that from the procedural point of view, the *chemical* composition of the rocks and the open or closed character of natural systems are related to different philosophical categories of indications. Chemical composition is in the category of external indications and the open or closed character of natural systems is a category of the internal state of the systems. The defining element in uniting them is that of the indications related to the category of internal (internal state), i.e., genetic, indications. On the basis of the open or closed character of natural systems, it is possible to consider the iso- or allochemistry of processes in regional metamorphism. On the other hand, however, it is impossible to evaluate the open or closed nature of the systems based on a comparison of average rock compositions. This type of procedural error is extremely common [11, 18, etc.].

Example 2. The work of B. V. Petrov and V. A. Makrygina [14] is a monographical study devoted to the geochemistry of regional metamorphism and ultrametamorphism in rocks of the Baikal-Patom highlands. It treats a number of extremely important questions associated with the study of regional metamorphism and attempts to consider the deficiencies or previous investigations of this type and, insofar as possible, to avoid these in practice. A great deal of attention is devoted to the general statement of the problem of the presence of lack of isochemistry in regional metamorphism and the methods for solving them. "There are two ways to solve the problem stated" write Petrov and Makrygina. "The first is a statistical treatment of the analyses published in the literature... Several works of this type are known [1, 8, 10, etc.]...The second way is more promising. It consists of directly tracing and sampling one or more strata in different metamorphic zones. With this approach, it is quite unimportant what the rocks being studied are called. The main point is that the strata be transitional from one metamorphic zone to another...The difficulty in interpreting the results of the second method of studying the isochemistry problem lies in the necessity for considering lithological factors, which, along with metamorphism, may be the cause for change in the chemical composition of the rocks along the strata. However, this difficulty can be overcome [14, pp. 5-6]. The authors' main conclusion is reduced to the following position: "It is proven that progressive regional metamorphism is inert in relation to the majority of petrogenic and trace elements and is sufficiently close to an isochemical process" [14, p. 323].

"These authors see the principal difference between their investigations and other works of a similar design as being primarily in the selection of areas which served as the basis for a study of metamorphic processes. The main requirements which they set forth for the choice of areas are: 1) the presence of 'crosscutting' metamorphic or metasomatic zoning; 2) a broad assemblage of original rocks; 3) a considerable range of thermodynamic conditions; 4) exposure sufficient to trace and sample the horizons selected in all the metamorphic zones. For each of the areas, detailed geological and metamorphic maps were drawn, mineral associations are analyzed in all the very widespread varieties of rock, and their major lithologic characteristics are presented" [14, p. 323].

In spite of the broad coverage of questions associated with solving the isochemistry problem in regional metamorphism, there are essentially important omissions in the work cited. Since we are speaking of the behavior of petrogenic elements in a process (in this case, the process of regional metamorphism), the main requirement set for selecting areas for investiga-

tions of this type is not the set of requirements enumerated by Petrov and Makrygina, but the possibility of answering questions of time and above all the possibility for a well founded reconstruction of the sequence of metamorphic mineral formation. It is expedient to concentrate all our attention on this extremely important and at the same time painful question in studying metamorphism.

In connection with the fact that the evolution of mineral composition is in the form of an exchange of mineral parageneses, it is necessary (to avoid omissions) to point out how the authors themselves understand this extremely important term, e.g., according to D. S. Korzhinskii and others. Judging from the data presented, associations are at least considered to be simultaneously formed minerals. If so, then the separation of mineral parageneses must be confirmed by indications of their simultaneous formation. However, in the case of metamorphic rocks, criteria of this type have still not been developed. In this case, to what are the proofs of mineral paragenesis reduced in the monograph of Petrov and Makrygina? They themselves write as follows on this, for example: "Interrelationships between kyanite and chloritoid show that they are paragenetic (Fig. 6)" [14, p. 29]. And that's all! The figure indicated proves nothing except that in high-alumina schists, kyanite and chloritoid occur together and that the size of the kyanite crystals is considerably greater than that of chloritoid. Fine structures of coincident growth are needed, from which their simultaneous formation would unequivocally result. There is no criterion for mineral paragenesis or the absence of reaction interrelationships. The fact of the matter is that in this case, it is impossible to separate the paragenetic minerals from the stable ones! How did the authors of this monograph overcome these objective difficulties? We read: The formation of kyanite must obviously have been through the reaction of pyrophyllite $\rightarrow$ kyanite + quartz + H_2O . Confirmation of this is in the noticeable increase in quartz content in the subfacies rocks, while the amount of chloritoid and muscovite remained at its former level" [14, p. 28]. There is not "confirmation" here, just a procedural error, the essence of which is reduced to the fact that by the criterion of the internal development of a system, i.e., the origin of the kyanite, features are introduced which belong in the category of external indications (the quantitative relationships of the minerals). In a subsequent statement, in solving the problems of formation for one mineral or another, Petrov and Makrygina were led on by the same erroneous criterion, with the difference that in isolated cases they indicate the hypothetical character of the reactions presented. For instance, "The magnesian content of biotite from these rocks [calcareous-silicate - I.B.] is comparatively high...therefore, its formation cannot be according to the usual reaction of chlorite + sericite + ankerite $\rightarrow$ biotite + calcite + H_2O + CO_2 . The notable reduction in the amount of ankerite in the biotite zone serves as confirmation of this" [14, p. 80]. And further on: "In ferruginous schists...judging from the change in mineral relationships in the rocks, a hypothetical reaction for biotite formation is chlorite + muscovite + chloritoid $\rightarrow$ staurolite + almandine + biotite + H_2O ." In conclusion, let us consider the formation of epidote. The authors attempt from the very beginning to convince the reader that "their field of stability [for minerals in the epidote group - I.B.] is spread over all the metamorphic facies studied" [14, p. 103]. But perhaps epidote simply is a regressive mineral and, being formed in rocks of all the facies "studied," creates the illusion of stability under a wide range of thermodynamic conditions. Here is what Petrov and Makrygina write regarding this reason: "In a number of cases, actually, it may be observed how common epidote is developed along late cracks in the rock. However, this in no way serves as proof that all the epidote with the usual composition is secondary. On the contrary, a number of facts, including features of the chemical composition of epidote, concern its equilibrium with other coexisting minerals in amphibole rocks" [14, p. 105]. And furthermore: The alteration in the petrographic composition of calcareous-silicate rocks...confirms that the formation of epidote proceeds according to the reaction muscovite + chlorite + carbonate $\rightarrow$ biotite + epidote + CO_2 + H_2O ." It has been stated above that the change in the petrographic composition (the quantitative relationships of the minerals) cannot be evidence of mineral formation. It is unclear what is hiding behind the series of facts; something else is clear...features of the chemical composition of minerals, in this case epidote, cannot concern its equilibrium with other minerals. We, as geologists, are not able to prove simultaneity of mineral formation in thin sections (if, of course, we are governed by objective criteria), but the proof of mineral equilibrium is still the aim, difficult to perceive, of investigators working in the area of reconstructing metamorphism.

These examples, it is true, are sufficient to explain that questions of time, on which depend the conclusions of the work being produced, have remained insoluble. The mineral parageneses isolated by Petrov and Makrygina [14, pp. 29, 30, 72, etc.] are no more than *hypothet-*

ical parageneses: the reconstruction of a sequential shift in mineral parageneses over time also bears the same hypothetical character. All this, taken together, alters the essence of the matter, i.e., the degree of basis for the main conclusion concerning the isochemistry of processes in progressive regional metamorphism, which is transformed from a proof to a hypothetical indication, in other words, to a hypothesis, which, if the entire assemblage of assumptions is taken into consideration, is not very likely. Finally, there is no control of the investigation's results by independent methods. The works cited are no exception. They provide a general descriptive notion that a study of the chemistry of regional metamorphic processes have only just begun, in essence. Without solving the problems of time, under other favorable circumstances, there can be no solution to the problem of isochemistry or lack of it in the processes of regional metamorphism.

There is one more variant in reconstructing the nature of metamorphic rocks, based on the rock chemical data presented by A. A. Marakushev and V. I. Fel'dman [12]. The basis of the method is preceded by a brief characterization of the processes of metamorphism with the mention that in certain cases, metamorphism is accompanied by substantial change in chemical composition, which makes difficult or impossible the reconstruction of the original nature of the metamorphic rocks, while in other cases, alteration of the composition of components other than volatile ones is not very significant and can be neglected in the course of rock chemical calculations. The main thing, from the viewpoint of these authors, is the question of delimiting the ortho- and parametamorphic rocks...a question upon which all their attention is concentrated. A general summary of the work is that reconstruction of the original nature of metamorphic formations is a problem *solvable in relation to rock chemistry* only on the basis of comparing their chemical compositions with the compositions of the major types of sedimentary and volcanic rocks. The diagrams presented in the article for such a comparison are effective only if they are used together and when entering on them not unique random analyses of metamorphic rocks but sufficiently representative data on rock chemistry. It is hard to agree with the summary of Marakushev and Fel'dman, since coverage of the compositions of ortho- and parametamorphic rocks is not a unique and definitive deficiency which stands in the way of introducing a rock chemical method into practice in reconstructing the nature of metamorphic rocks.

As is well known, the recognized distinction between different types of sedimentary and igneous rocks is at the basis of rock chemical methods for reconstructing the nature of metamorphic rocks. Since the chemical composition of rocks is related, from the procedural point of view, to the category of external indices for geological objects, i.e., those which do not uniquely define its essence,* all the deficiencies of this criterion "migrate" into rock chemical methods. Moreover, having extended their sphere of applicability to the Precambrian, investigators have automatically introduced new deficiencies to these methods; the negative value of the latter is exceeding that permissible in geology. Therefore the rock chemical methods must, in their modern form, inevitably be in contradiction to the logic of our understanding and to scientific facts. With the development of mutually controllable methods for reconstructing the nature of ore matter in Precambrian iron formations, the nature of contradictions has been exposed to an even greater extent. First of all, this is a contradiction to the demands of dialectical logic, manifested primarily in ignoring time in all of its very important aspects (geohistorical and evolutionary metamorphic). One of the major internal contradictions in rock chemical methods is the need to throw out rocks which have undergone substantial influx or efflux of matter, which, as was shown above, means the liquidation of the rock chemical method itself. One of the major external contradictions is that of the results of reconstructing the premetamorphic and original nature of ore matter in Precambrian iron formations [2-6, 22, etc.], which show that deposition of ore matter in these formations took place in the form of *chemical* iron carbonates, that the Precambrian was distinguished by a reducing carbon dioxide atmosphere, and that consequently the nature of exogene processes in the Precambrian must have differed substantially from the character of these processes in the Phanerozoic. Therefore, there must have been no extratemporal, "absolute" rock chemical methods (or classification). Its own peculiar standard rock-chemical information must be introduced for the Precambrian.

*Thus, for instance, according to Marakushev and Fel'dman, a partial coincidence of compositions is noted for basic rocks, clay-carbonate rocks, gabbros, and diorites with hydromica and montmorillonite clays, and in part with graywackes and for granites with graywackes and arkoses [12].

Let us recount several principally important deficiencies peculiar to rock chemical methods: 1) they do not permit the reconstruction of the nature of metamorphosed rocks which have disappeared in the geological history of the earth; this involves primarily the nature of shale-ore matter in Precambrian iron formations, i.e., magnesian-iron and iron carbonates; 2) they do not offer the possibility of differentiating rocks of the same composition but different origin (such as chemical dolomites and replacement dolomites after limestone, chemical siderites and diagenetic or hydrothermal siderites, etc.), which is extremely important in understanding conditions of exogene rock formation in the Precambrian; 3) they do not permit in full measure the reconstruction of the volume of calcareous-magnesium carbonates in the Precambrian; 4) they do not offer the possibility of reconstructing the valence forms of the elements in unmetamorphosed matter and of thereby evaluating the evolution of elemental valence forms in the processes of metamorphism.

In other words, applying rock chemical methods leads to the extinction of evolutionary elements in the geological history of the earth.

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The set of cryogenic dislocations in Recent sediments of cryolithic zones are described: disruptive and plicative. Plicative dislocations are varied and are produced by two main mechanisms: 1) local intrusions (injections) of groundwater and quicksand grounds into rock strata frozen on the top, giving rise to anticlinal structures or groups of such structures, which may or may not be expressed in the existing terrain topography; and 2) area plicative dislocation of the strata of finely dispersed waterlogged sediments in basins as they freeze from the top while surrounded by aquicludes (including permafrost rocks) at the bottom and on the sides.

Sedimentary rocks of recent and ancient cryolithic zones — the zones with perennially frozen beds and ground ice — experience all kinds of plicative and disruptive dislocations. These can be divided into three main groups according to their origin: lithogenic, glaciogenic, and cryogenic. Lithogenic dislocations occur during sediment accumulation and during diagenesis. These are typically structures resulting from slumps and landslides of bottom waterlogged grounds or convective structures ("burdens"), which sometimes attain a large size, measuring tens of meters in the vertical direction [3]. In addition, in areas of past or current glaciation all kinds of glaciogenic dislocations are possible due to the action of ice upon underlying rocks, as well as processes forming the ice deposits [6, etc.].

The present paper is concerned with cryogenic dislocations caused by the freezing of sediments and underground ice formation. Morphologically, they are often similar to lithogenic and glaciogenic dislocations. They should be differentiated from those, however, to reconstruct the sedimentation environments of the past and to diagnose the ancient areas where permafrost rocks and ground ice could have existed. It is well known today that cryogenic sedimentation settings existed in virtually all areas of the Phanerozoic, the early and late Proterozoic, and possibly the late Archean. The importance of correct identification of cryogenic dislocations and the description of their typical features to distinguish them from glaciogenic, lithogenic, and true tectonic processes is obvious.

Cryogenic dislocations exhibit a remarkable similarity (sometimes on a different scale) with the familiar tectonic dislocations, both of disruptive and of plicative type. Studying them in that respect is essential for understanding all aspects and features of tectonogenesis, including the cryogenic processes. The diversity, commonness, and specifics of permafrost dislocations, as will be shown below, give grounds to speak of a separate type of exotectogenesis — cryogenic tectogenesis. Cryogenic dislocations, however, have not been described adequately in special lithologic publications.

DISRUPTIVE CRYOGENIC DISLOCATIONS

Disruptive cryogenic dislocations are formed by frost, cracking of grounds due to steep winter cooling, and volumetric reduction. Intersecting frost cracks are formed (Fig. 1A), giving rise to polygons, mostly tetragons, seen clearly in the surface topography. Given a certain combination of conditions — a sufficient moisture content and finely dispersed, especially peat-filled, soils — the cracks "heal" with ground ice. The frost cracking and ice healing recur cyclically, producing underground vertically oriented wedge-shaped ice veins (Fig. 1B). The vertical size of these cracks can be 12–15 m; they are 3–5 cm wide. If the frost cracking and ice vein formation occurs against the background of an intensive continental accumulation in low-lying regularly flooded laydas, deltas, and at the feet of gentle slopes, ice veins up to 8–10 m wide and of a vertical size of 40–60 m and more can be formed, because the permafrost-cryogenic process evolves in parallel to the sedimentary

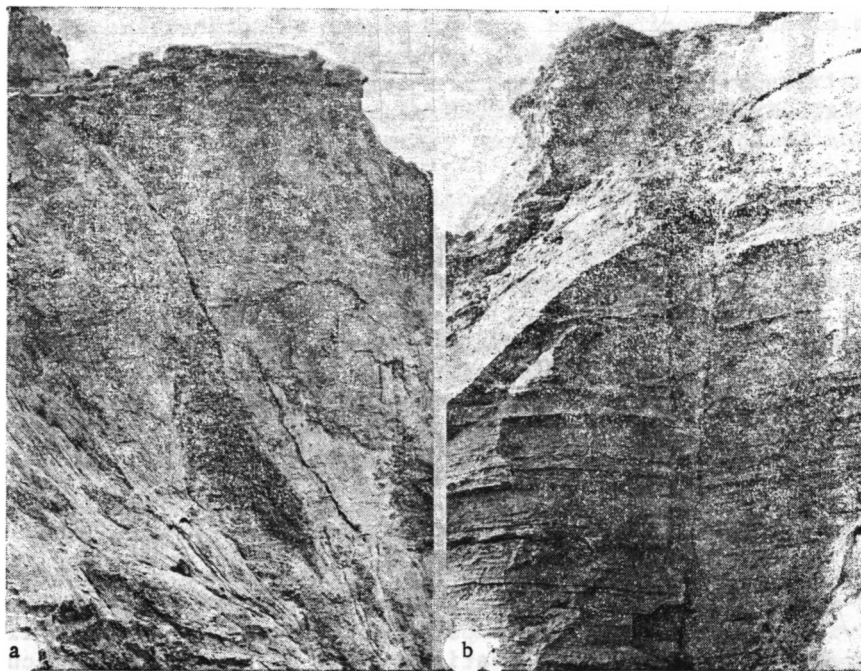


Fig. 1. Frost crack and ice vein with a small displacement of stratified rocks of a basin genesis traceable along them: (A) frost crack, partly "healed" with ground ice, penetrates a bed of stratified siltstones to a depth of 15 m beneath the day surface; (B) the ice vein of a visible vertical size of 3.5 m formed as a result of "healing" of a series of frost cracks with ground ice.

process. Often no ice veins are formed along the frost cracks, but rocks are displaced along them. The displacement of rock layers can also be observed along ice veins (see Fig. 1B).

PLICATIVE CRYOGENIC DISLOCATIONS

Plicative cryogenic dislocations are diverse in terms of morphology and formation mechanism. One can distinguish local structures associated with intrusions (injections) of water or water-ground masses into perennially or seasonally frozen beds and fold dislocations, which have an area occurrence associated with stresses caused by the freezing of beds and layers of waterlogged finely dispersed (quicksand) soils.

Of an undoubted cryogenic origin are the dislocations in so-called frost mounds, which are relatively large local anticlinal structures. They are particularly distinct in multi-annual frost mounds, which in Yakutia are called bulgunnyakh, and in the northern part of North America are known as pingo. The frost mounds are up to 50-70 m in height with a diameter of 100-150 m and more. Inside the mound is an ice core that forms the central part of the structure; above the core, permafrost rock layers are bent conformally into anticlinal folds.

The internal structure of a mound bears morphological traits of intrusion (injection) of frozen water or water-soil mass into enclosing rocks, which by the time of injection were already frozen but yet experienced a plastic deformation without any disruption of continuity.

The development of large perennial frost mounds is due to the freezing of locked volumes of thawed waterlogged ground under the bottom of drained lake basins. The freezing creates thaw bowls surrounded by frozen rock. As the size of the bowl contracts, tremendous hydrostatic pressures are produced. The pressures are relaxed by squeezing out waterlogged ground and groundwater in the direction of least resistance, i.e., usually upward. Mounds with ice cores and associated folded dislocations are thus formed, dislocations shaped as anticlinal structures.

In addition to anticlinal structures of frost mounds of a doubtless cryogenic nature, seen in the existing relief, there are anticlinal structures in permafrost beds that are not

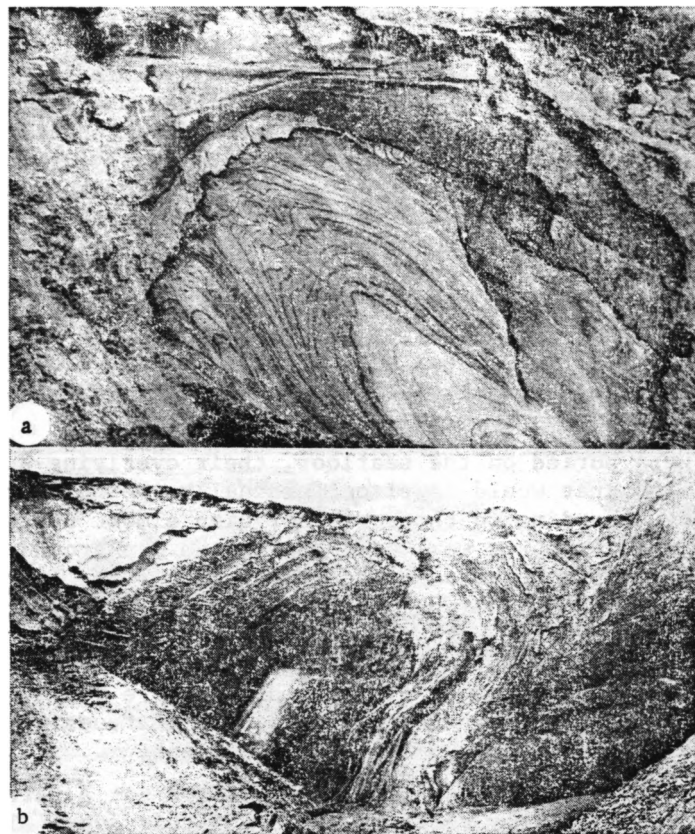


Fig. 2. Anticlinal structures formed by intrusions of ground ice and ice-ground into beds of stratified basin sand-clay-silt sediments: (A) large anticlinal structure of the visible vertical size of about 7 m formed by layered ground ice; (B) a system of two interconnected anticlinal structures: left, intrusion of monolithic ice (white) and ice-ground (dark); right, ice-ground (dark).

expressed in the existing topography (Fig. 2). They are frequently taken for remains of ice dislocated by glacial movements and buried in the Pleistocene "originally frozen" sediments — these are relicts of glacier ice, former ice sheets of planes in cryolithic zones, etc. [4]. The cryogenic origin of these formations, however, is not established with full certainty.

The anticlinal structure shown in the photograph (see Fig. 2A) consists of ground ice saturated unevenly with air bubbles and mineral particles of pelitic, siltic, and psammitic fractions; in the former case, there are seen as white strips, in the latter as dark strips. The theory that a block of dislocated land glacier ice was buried cannot be accepted in this case for several reasons. First of all, it is the morphology of the anticlinal structure and its interior construction. The ice and its overlying rocks are clearly seen to be dislocated together. It is also obvious that the ice intruded upward stage by stage rather than being dislocated during horizontal movement in an ice sheet. The rocks enclosing the ice deposit are horizontally stratified ribbonlike siltstones of an obvious basin origin. Outside the structure they exhibit a normal horizontal bedding. There are not reasons to believe that the layer siltstones are an "originally frozen" moraine with blocks of plastically deformed glacier ice preserved in it.

A cryogenic rather than glaciogenic nature of underground dislocated ice deposits is demonstrated even more convincingly by another example (see Fig. 2B). The photographs shows two intrusions shaped as anticlinoria with ice cores inside; the ice cores consist of very strongly deformed ice and ground mass and monolithic ice connected with it. The ground portion of the mix consists of viscous, sometimes almost black oozy siltstone with a pungent odor of decaying organic matter. They contain rare inclusions of coarse clastic material, mainly pebble, scree, and less often small boulders. Monolithic ice is inhomogeneous and in various bodies consists of modification: pure, glasslike, white sugarlike (filled with air bubbles), and dirty (with mineral particles).

The layered sandstones and silts covering the ice core are bent in conformity with its shape; the slope angles on the sides are up to 45° and some of the folds are overturned. The total thickness of rocks involved in the dislocation visible in natural sections is 20-30 m; their true thickness is certainly greater. The dislocations are not expressed in the present relief and are cut by an even, almost flat surfaces of terracelike topography levels. The transition of the ice core of the structures into the overlying rocks is gradual: unstratified iced oozy silt up the profile gives way, first, to fine horizontally layered and then band-layered sandy siltstone, which gradually goes over into a bed of sands — first, small-grained horizontally stratified, and then medium-grained wavy sloped and obliquely stratified. All the lithologic varieties of rocks contain foraminiferal microfauna complexes; the icy ground of the core contains, in addition, shells of marine mollusks. The stratified sands, siltstones, and the ground components of the dislocation ice core were therefore accumulated in a sea environment. If one could speak of the burial of ice blocks, that burial would have occurred on the floor of a sea basin. This hypothesis, however, is contradicted by several observations.

If ice blocks were buried on the seafloor, their overlying sediments would have an enveloping stratification that would level out gradually up the section. Yet the layers covering the core are bent according to the core roof with almost unchanged thickness; in other words, layers of marine sediments were bent as ice and ice-ground intruded into them, rather than being formed as ice blocks were buried on the seafloor. In the environment of a water basin bottom, with a high water saturation, the sand and silt layers would be incapable of remaining on a slippery surface of an ice body at an angle of 45° , not to mention their being included in overturned folds. The morphology and construction of these structures definitively indicate that they were formed due to a growth of the core rocks, as ice (with 70-80% of the rock volume) intruded into the beds during the course of freezing. The penetration of ice was accompanied by dislocation of the overlying sediments.

The large anticlinal structures with ice cores are not a rare phenomenon, but are common in permafrost beds of sedimentary rocks of the cryolithic zone. They are observed in areas with widespread shallow sea sediments of a sand-clay-silt composition (Northwestern Siberia, the Northern Siberian depression, and the coastal plains of Chukotka). The process of formation of ice intrusions apparently evolved as follows. First to be frozen after emerging above the level of the sedimentation basin were sandy subsurface sediments. As they froze, the water was squeezed down from the sands into calyey ooze — the familiar "piston effect" of moisture extrusion during the freezing of sandy beds. As a result, clayey ooze before it was frozen became waterlogged and converted to a quicksand condition. Its roof, i.e., the foot of the overlying bed, is always uneven. As a result, the ooze froze at different times in different locations, rather than simultaneously, forming closed systems with high hydrostatic pressures. The waterlogged quicksand masses were pushed upward by the high pressure into previously frozen beds and froze inside them, with an increase of the volume and a partial differentiation of matter into ice and ice-ground components. The degree of differentiation was determined by the speed of freezing and other factors as yet unknown. The underground ice intrusions, while causing anticlinal structures to be formed, were also dislocated themselves. The absence of manifest ice intrusions in the contemporary relief is due to its subsequent prolonged leveling by permafrost-denudation processes. The upward intrusion of matter in a semiviscous medium was probably also compensated by a downflow of material between neighboring anticlinal structures, which is clearly seen in a number of localities (see Fig. 2B).

Plicative folded dislocations which have an area occurrence and cover large stretches, are widespread and typical for frozen beds of the most recent sediments in the cryolithic zones. They are typical for stratified oozy sand, silt, and clay of a basin genesis. Folded area dislocations can either be lithogenic or cryogenic. Lithogenic dislocations are represented by various slump and downslope structures and convective structures (advective structures in Belousov's terminology [1]). The slide and slump structures are characterized by the following features in the strata of basin sediments: local occurrence, horizontal or oblique orientation, and series of intact or layered overlying sediments [2]. Convective (advective) structures range in thickness from a few centimeters to tens of meters and occur in a vertical section of sedimentary beds in several stories, alternating with layers of intact or slightly deformed rocks [3].

Fold dislocations encompass very thick (up to 40-60 m and more) beds of stratified basin sediments on long stretches of land measured by a few kilometers or even tens of kilometers. Their formation is attributed to underwater slumps or the action of ancient glaciers. However, these are indications that refute both of these theories.

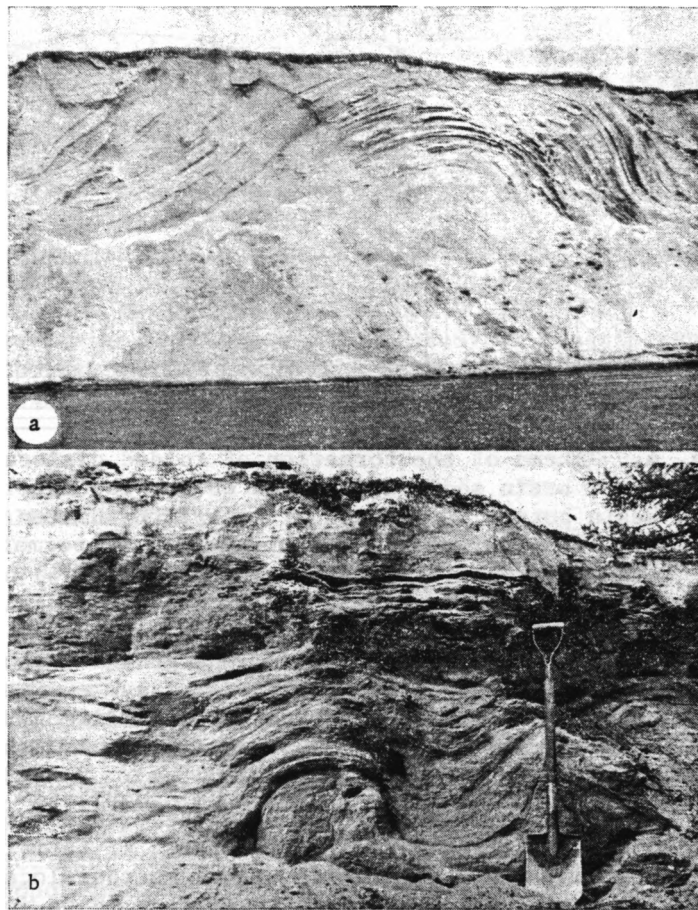


Fig. 3. Folded cryogenic dislocations: (A) large-scale dislocations in stratified small- and medium-grained sands of a visible thickness of approximately 20 m; (B) small size dislocations in the sands of summer-thawed and winter-frozen (active) layers.

A glaciogenic origin of these dislocations should be rejected for the following reasons. This mechanism assumes that the dislocations are of a glaciodynamic or glaciostatic nature. Either a glacier in its advance exerted a dynamic action on underlying stratified rocks of its bed, folding them, or it applied an uneven pressure to these rocks that had plasticity and were then extruded upward in sites of lower pressure. However, as with single anticlinal structures, the rocks dislocated into folds emerge to the day surface and are cut by it. They are not overlain by any other types of sediments, including those which could be classified as glacial, which would indicate that, in the past, stratified waterlogged beds were covered with glaciers. The surfaces formed by dislocated beds exhibit even and sometimes flat or terrace-shaped structures. If a glacier deformed plastic stratified water sediments, it ought to have also deformed the surfaces composed of them. No dislocations, however, appear in the relief. The glacial theory fails to provide a satisfactory explanation for the near coexistence of dislocated and nondislocated beds of different genesis within the same geomorphological surface and the existence of differently dislocated similar rocks within geomorphological levels at different altitudes.

The theory which attributes folded dislocations to underwater slumping or convective instability under uneven loads applied to waterlogged plastic grounds is also often unacceptable. This theory is contradicted by the joint dislocation of sediments and the ice interlayers and even beds of ground ice penetrating them observed in many locations. Recently, the submarine slumping of waterlogged bottom grounds and simultaneous ice separation in them have been explained by a different mechanism [5]. It has been established that bottom waters and sediments of polar seas are mainly of a negative temperature in the range from -1.3 to -1.8°C . The new theory suggests that the submarine slumping of sediments that would cause

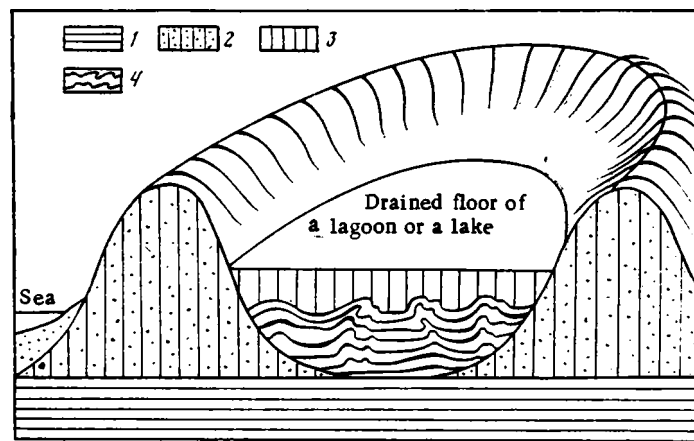


Fig. 4. Scheme of the formation of folded dislocations in beds of layered basin sediments frozen on the top after the sedimentation basin bottom is drained of water; the bottom is surrounded by elevated topographic forms consisting of permafrost rocks: (1) compacted rocks; (2) permafrost beds; (3, 4) newly formed perennially frozen rocks (3, undislocated; 4, dislocated).

their spontaneous separation into water component and ground component would cause free water to freeze at negative temperatures and bring the entire system into a frozen state. Attractive as this explanation of the combined dislocation of sediments and the ice included in them may seem, little justification has been provided for this new theory.

Cryogenic deformations caused by the freezing and volumetric changes due to underground ice separation seem to be the decisive factor in the development of folded dislocations in the basin sediments of the polar regions. The mechanism of formation of large cryogenic folded dislocations (Fig. 3A) can be clarified by the microdislocations of the so-called active layer (see Fig. 3B), i.e., the subsurface layer that thaws in summer and freezes in winter. The origins of the dislocations of the active layer can be determined with certainty and are due to the uneven depth of its autumn-winter freezing. The thawing depth in the summer is also uneven and depends on the relief, the vegetation, the thickness of the snow cover, etc. For the same reason the freezing in fall and winter also varies. As a result, when the active layer freezes, closed volumes of waterlogged thawed quicksand rocks are formed inside the layer, squeezed between the roof of permafrost and the base of rocks freezing from above. As the freezing process advances, the pressure rises in the closed interlayers of quicksand ground of the active layer over large areas. As a result, instead of local intrusions of groundwater and quicksand, an area dislocation of quicksand grounds occurs as they become frozen, accompanied by an overall rise (bulging) of the day surface.

Similar phenomena are observed when the bottom of a large sedimentation basin with waterlogged ooze becomes drained and dries out, with the ooze freezing over large areas (Fig. 4). The waterlogged layers of the basin ooze, underlain and bounded at the sides by dense (and sometimes frozen) rocks, begin to freeze intensely but unevenly from above, and closed systems of quicksand grounds are formed, with the pressure rising with continued freezing. The stresses cause the ooze layer to swell and be deformed plastically, similar to the active layer of the ground when it is frozen. Under certain conditions, local anticlinal structures with ice cores, described earlier, will be formed. On extensive areas bounded by previously frozen strata, the folded dislocation would occur on a broader horizontal plane. If no closed volumes with high pressures are formed during the course of freezing of the basin sediments, no dislocation of rocks will take place and they will become frozen without any substantial deformations.

All these data suggests that a special type of exotectogenesis exists in nature, which can be called cryotectogenesis. It is manifested in the development of disruptive and plicative dislocations. The latter are formed by two mechanisms: (1) local intrusions — injections of groundwater and quicksand into freezing sediment (anticlinal structures which may or may not be expressed in the existing topography); and (2) area folded-plastic deformation of waterlogged clay-silt ooze beds frozen from above when surrounded by aquicludes (including permafrost rocks) at the bottom and at the sides.

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A METHOD FOR STUDY OF CARBONATE OOZE

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UDC 551.351.3

Calcareous sediments have been established by numerous investigators to be quite common on the floor of the world ocean. In recent years, an important rock-forming role has been determined for the remains of calcareous nanoplankton. The term "Globigerina ooze" is becoming obsolete because, mostly, one is concerned with foraminiferal, foraminiferal-coccolithic and coccolithic-foraminiferal ooze. These names, however, are given on the basis of visual descriptions of sediment specimens or, at best, after their investigation in a binocular microscope at small magnifications. In view of the micrometer sizes of nanofossils, the early conclusions concerning sediment composition are often unreliable. At magnifications of up to 100, the quantitative proportions of fine-walled foraminiferal chambers and minute coccoliths are hard to estimate, especially since coccoliths stick to the outside surfaces and often fill the chambers, sometimes completely. The granulometry of the noncarbonate component is also often disregarded.

TABLE 1. Principal Rock-Forming Components of Seafloor Sediments from the Vim Fault (station 4072)

Horizon, cm	Granulometry		CaCO ₃	Foraminifera	Coccoliths	Sand	Silt	Pelite
	Class	%						
65	Sand	78	95	74	—	4	—	—
	Silt	12	72	—	8.6	—	3.4	—
	Pelite	10	50	—	5	—	—	5
	Coccolithic-foraminiferal clayey ooze							
170	Sand	42	95	40	—	2	—	—
	Silt	27	97	—	26	—	1	—
	Pelite	31	81	—	25	—	—	6
	Foraminiferal-coccolithic clayey ooze							
285	Sand	32	97	31	—	1	—	—
	Silt	37	98	—	36	—	1	—
	Pelite	31	85	—	26	—	—	5
	Foraminiferal-coccolithic clayey ooze							

*Sand content is slightly overestimated due to the presence of finely dispersed noncarbonate impurity in foraminiferal chambers.

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TABLE 2. Principal Rock-Forming Components of the Seafloor Sediments in the Atlantic

Site number	Hori- zon, cm	Granulometry		CaCO ₃	Fora- mini- fers	Cocco- liths	Sand	Silt	Pelite
		Class	%						
Vernadskii fault									
4243	50	Sand	85,5	99	84,6	—	0,9	—	—
		Silt	13,3	60	—	8	—	5,3	—
		Pelite	1,2	—	—	—	—	—	1,27
		Coccolithic-foraminiferal ooze, silty							
Josephine Bank									
4002	4—9	Sand	20	85	17	—	3	—	—
		Silt	47	58	—	27,3	—	19,7	—
		Pelite	33	47	—	15,5	—	—	17,5
		Foraminiferal-coccolithic clayey-silty ooze							
	40—44	Sand	20	73	14,6	—	5,4	—	—
		Silt	40	43	—	17,7	—	22,8	—
	Pelite	40	28	—	11,2	—	—	28,8	
	Foraminiferal-coccolithic silty-clayey ooze								
Ampere Bank									
4003	3—8	Sand	19	38	7,2	—	11,8	—	—
		Silt	42	34	—	14,3	—	27,7	—
		Pelite	39	29	—	11,3	—	—	27,7
		Foraminiferal-coccolithic silty-clayey ooze							

To avoid subjective biases in classifying calcareous ooze and to introduce elements of quantitative analysis, we have suggested a method which made it possible to use the results of granulometric analysis and determinations of the carbonate content of sediments, normally done as part of field descriptions in onboard laboratories.

The method is based on data of microscopic investigations, suggesting the major role in pelagic carbonate sediments for two components: fragments and whole shells of planktonic foraminifers and mineral remains of calcareous nannoplankton. Aragonitic fragments of pteropod shells rarely play a significant role on submarine rises in the equatorial and subtropical oceans.

Since foraminifers and their fragments are larger than nanofossils by one or two orders of magnitude, one gets the subjective impression that the sediment is largely foraminiferal even when nannoplankton remains are in fact predominant.

Our method is based on the differences in the size of these organogenic remains. The carbonate part of the pelitic fraction (<0.004 mm) consists entirely of nannoplankton fragments. The silt fraction (0.004–0.05 mm) largely consists of nannoplankton remains in its carbonate component. Small foraminiferal fragments also occur here, but their content is small and is offset by a presence of nannoplankton in foraminiferal chambers, which are predominant in fractions of over 0.05 mm. By determining the carbonate content in each of the three fractions it is thus possible to recalculate them into the main rock-forming organogenic and nonorganogenic components (clay minerals and terrigenous admixture). The content of the latter is defined after subtracting carbonates from each fraction.

The procedure is illustrated by the results of investigations from various stations during leg 28 of *Akademik Vernadskii* research vessel (Tables 1 and 2).

The analytical data in the tables show that in the pelagic regions of the Atlantic coccolithic-foraminiferal and foraminiferal-coccolithic ooze varieties are ubiquitous. Even when a sediment seems to be a typical "foraminiferal sand" when observed under an MBS binocular lens, it turns out to be at least 8–10% nannoplankton remains. The true "foraminiferal sands" are apparently a rare formation in the pelagic part of the ocean, which indicates an intensive

hydrodynamic rewashing of seafloor sediments, rather than their primary composition. Such re-washing is more likely on submarine rises, whose tops come close to the water surface and are exposed to wave and surf activity.

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